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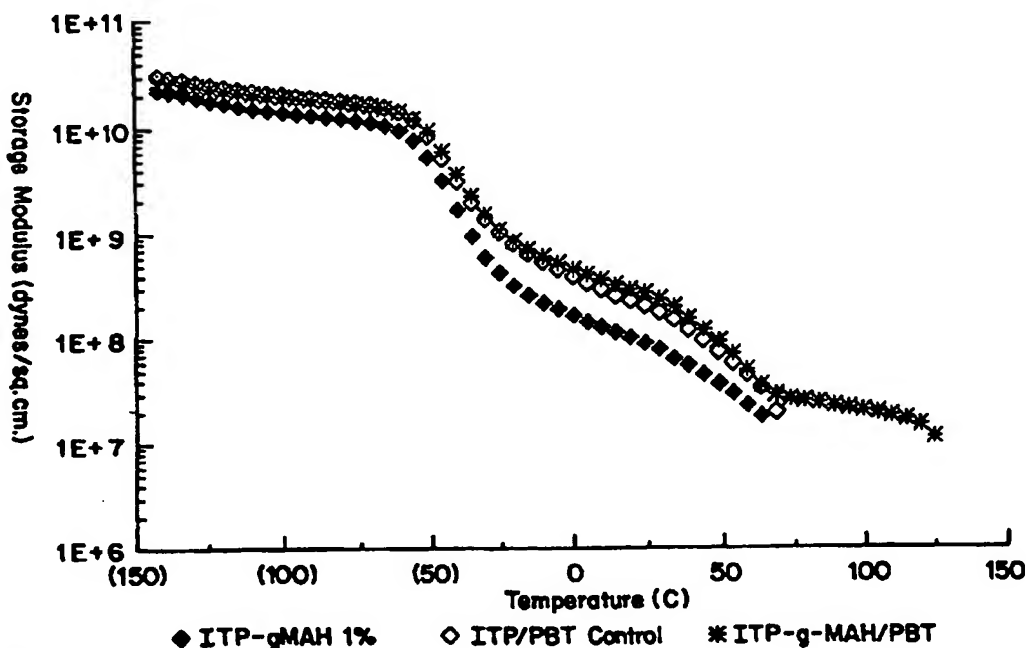
(57) Abstract

Branched block ethylene polymers prepared from a narrow ethylene polymer, an ethylenically unsaturated functionalized organic compound, and reactive thermoplastic polymer, and methods of preparing such branched block ethylene polymers, are useful to prepare an impact modified ethylene polymer.

rubbers such as ethylene/propylene copolymer. These added substances
are capable of improving the resistance of polycarbonate to solvents,
but they tend to delaminate and cause an offsetting reduction in the
toughness, impact resistance and weldline strength of the blended
5   polycarbonate composition. Such delamination, and the resulting loss
of utility, is reported, for example, in US-A-4,496,693.

Impact resistance in polycarbonate can be improved by the
incorporation of emulsion or core-shell elastomers such as
methacrylate/butadiene/styrene copolymer or a butyl acrylate rubber.
10 However, these core-shell rubbers hinder processability of the blend
by increasing viscosity, and impart no improvement to the solvent
resistance of polycarbonate. It would accordingly be desirable if
modifers, particularly olefin-based modifiers, blended with
thermoplastics such as polycarbonate for the purpose of improving
15 solvent resistance did not also deleteriously affect toughness and
impact and weldline strength, and cause delamination as evidenced by
peeling or splintering in a molded article.

US-A-5,346,963 discloses ethylene polymers which are grafted
with an ethylenically unsaturated compound, and discloses blends of
20 such grafted ethylene polymers with compatible thermoplastics. The
description of the graft-modified ethylene polymers in this reference
does not, however, mention a branched block ethylene polymer as
defined herein.

US-A-5,300,574 discloses that crosslinking is reduced when
25 maleic anhydride is grafted onto a saturated ethylene polymer if the
grafting reaction is conducted in the presence of a polyamide.
However, this reference does not mention a branched block ethylene
polymer.

30   Hughes, et al. in U.S. Patent 5,346,963 disclose substantially
linear polyethylenes grafted with one or more unsaturated organic
compounds containing both etheneic unsaturation and a carbonyl group
in thermoplastic blends as compatibilizers for filled polymers, and as
impact modifiers for other polyolefins and a polyamide.
35

BRANCHED BLOCK ETHYLENE POLYMERS, THEIR PREPARATION AND COMPOSITIONS
COMPRISING THE SAME

Field of the Invention

5   This invention relates to ethylene polymers, more specifically
block polymers of ethylene polymers, compositions containing block
ethylene polymers, methods for the preparation of such block ethylene
polymers and for compositions containing such block ethylene polymers.

10

Background of the Invention

        The graft-modification of an ethylene polymer with various
olefinically unsaturated monomers is well known in the art. Such
15   modification renders an essentially nonpolar polymer material
compatible, at least to some limited extent, with a polar material.

        However, graft-modification can have a detrimental impact on one
or more other properties of an ethylene polymer. For example, USP
20   4,134,927, 3,884,882 and 5,140,074 all report undesirable changes in
rheological properties due to cross-linking of a graft-modified
material. These changes ultimately impact the processibility of the
material and, thus, its utility in commercial applications.

25   In addition, when it is desired to blend an ethylene polymer
with another molding polymer, graft-modification of the ethylene
polymer, which may be beneficial in the context of adhesiveness, may
adversely affect the compatibility of the ethylene polymer with the
blending or molding polymer. It would accordingly be desirable if an
30   ethylene polymer could be modified in such manner that its
compatability with other polymers in a blend is not adversely affected
while other properties of the ethylene polymer (and preferably the
resulting blend), such as its rheology, are improved.

        An additional and particular challenge which has confronted
35   industry is the improvement of the properties of polycarbonate. This
disadvantage has been somewhat relieved by the practice of blending
polycarbonate with various olefin polymers such as low density
polyethylene or linear low density polyethylene, or thermoplastic

1

a reactive thermoplastic polymer capable of reacting with the
ethylenically unsaturated organic compound, said method comprising

(1)   forming the ethylenically unsaturated functionalized organic
5   compound into a branch off of the ethylene polymer to form a
       branched ethylene polymer, and thereafter

(2)   reacting the reactive thermoplastic polymer with the branched
       ethylene polymer to form the branched block ethylene polymer.

10   In a preferred aspect, this invention involves a method of
preparing a branched block ethylene polymer which comprises

(a)   a homogeneous ethylene polymer which preferably has:

       (i)   a M_w/M_n ratio, as determined by gel permeation
               chromatography, of less than about 3.0;

15   (ii)   a density of about 0.93 g/cm^3 or less; and

       iii)   a Short Chain Branching Distribution Index of greater
               than about thirty percent;

(b)   an ethylenically unsaturated functionalized organic compound;
       and

20   (c)   a reactive thermoplastic polymer capable of reacting with the
              ethylenically unsaturated functionalized organic compound;

said method comprising (1) forming the ethylenically unsaturated
functionalized organic compound into a branch off of the homogeneous
25   ethylene polymer to form a branched homogeneous ethylene polymer, and
thereafter (2) reacting the reactive thermoplastic polymer with the
branched homogeneous ethylene polymer to form the branched block
ethylene polymer.

30   In yet another aspect, this invention involves a composition
comprising a blend of a thermoplastic blending or molding polymer with
a branched block ethylene polymer, wherein the branched block ethylene
polymer comprises

(a)   an ethylene polymer;

35   (b)   an ethylenically unsaturated organic compound; and

4

One of the objects of this invention is to prepare an ethylene-based polymer which has improved viscoelastic behavior, and which, when used as a modifier in a blend with a thermoplastic molding polymer, imparts to such blend a desirable balance of improved

5   rheological behavior, good impact resistance, transparency in thin sections and films, surface hardness, and reduced notch sensitivity. This object, and others disclosed below, is attained by the preparation of a branched block ethylene polymer and the use of such branched block ethylene polymer in the compositions of this invention.

10 Summary of the Invention

In one aspect, this invention involves a branched block ethylene polymer comprising

(a)   an ethylene polymer;

(b)   an ethylenically unsaturated functionalized organic compound;

15   and

(c)   a reactive thermoplastic polymer capable of reacting with the ethylenically unsaturated functionalized organic compound to form the branched block ethylene polymer.

20 In a preferred aspect, this invention involves a branched block ethylene polymer comprising

(a)   a homogeneous ethylene polymer having:

(i)   a M_w/M_n ratio, as determined by gel permeation chromatography, of less than about 3.0;

25   (ii)   a density of about 0.93 g/cm^3 or less; and

(iii)   a Short Chain Branching Distribution Index of greater than about thirty percent;

(b)   an ethylenically unsaturated functionalized organic compound; and

30 (c)   a reactive thermoplastic polymer capable of reacting with the ethylenically unsaturated functionalized organic compound to form the branched block ethylene polymer.

In another aspect, this invention involves a method of preparing

35 a branched block ethylene polymer which comprises an ethylene polymer, an ethylenically unsaturated functionalized organic compound and

3

determined by gel permeation chromatography, of less than about 3.0, a
density of about 0.93 g/cm^3 or less; and a Short Chain Branching
Distribution Index of greater than about thirty percent; an
ethylenically unsaturated functionalized organic compound; and a
5   reactive thermoplastic polymer, said method comprising:

(1)   forming a branched block ethylene polymer by
      (a)   adding the ethylenically unsaturated functionalized
            organic compound to the homogeneous ethylene polymer to
10   form a branched homogeneous polymer, and thereafter
      (b)   reacting the reactive thermoplastic polymer with the
            branched homogeneous ethylene polymer to form a branched
            block ethylene polymer; and thereafter

(2)   blending the branched block ethylene polymer with the
15   thermoplastic blending or molding polymer.

In one preferred aspect, the reactive thermoplastic polymer of
component (c) will be an amine-functionalized polymer. In another
preferred aspect, the reactive thermoplastic polymer of component (c)
20   will be a polyester.

Surprisingly articles molded from the compositions of this
invention show advantageous temperature storage modulus in excess of
that exhibited by either a blend of corresponding polymers described
25   in (a) and (c) [hereinafter (a)/(c)] or polymer (a) grafted only with
(b) [hereinafter (a)/(b)]. That is, the branched block ethylene
polymers of the invention soften and deform at higher temperatures,
i.e. they exhibit a greater upper service temperature than (a)/(c)
blends or (a)/(b) grafts. Also the branched block ethylene polymers
30   of the invention show a surprisingly lower Tan Delta than that of the
(a)/(b) grafts or (a)/(c) blends.

Figures 1-18 are graphs (charts). Figure 1 shows the storage
modulus of a branched block ethylene polymer of the invention
35   (designated ***) compared with controls which are not examples of the
invention. Figures 2a and 2b are DMS Rheology Comparisons of branched

6

(c)   a reactive thermoplastic polymer capable of reacting with the
       ethylenically unsaturated organic compound.

       In a preferred embodiment, this invention involves a composition
5   comprising a blend of a thermoplastic blending or molding polymer with
       a branched block ethylene polymer, wherein the branched block ethylene
       polymer comprises
       (a)   a homogeneous ethylene polymer which has:
              (i)   a M_w/M_n ratio, as determined by gel permeation
10   chromatography, of less than about 3.0;
              (ii)   a density of about 0.93 g/cm^3 or less; and
              (iii)   a Short Chain Branching Distribution Index of greater
                      than about thirty percent;
       (b)   an ethylenically unsaturated organic compound; and
-15   (c)   a reactive thermoplastic polymer capable of reacting with the
              ethylenically unsaturated organic compound.

       In yet another aspect, this invention involves a method of
       preparing a composition from a thermoplastic blending or molding
20   polymer, an ethylene polymer, an ethylenically unsaturated
       functionalized organic compound; and a reactive thermoplastic polymer,
       said method comprising:

       (1)   forming a branched block ethylene polymer by
25   (a)   adding the ethylcenically unsaturated functionalized
                     organic compound to the ethylene polymer to form a
                     branched ethylene polymer, and thereafter
              (b)   reacting the reactive thermoplastic polymer with the
                     branched ethylene polymer to form a branched block
30   ethylene polymer; and thereafter

       (2)   blending the branched block ethylene polymer with the
              thermoplastic blending or molding polymer.

       In a preferred aspect, this invention involves a method of
35   preparing a composition from a thermoplastic blending or molding
       polymer; a homogeneous ethylene polymer which has a M_w/M_n ratio, as

shows how the melt strength is improved by the addition of various
percentages of Nylon 6 to MAHg8200. Figure 15 shows the effect of oil
on viscosity of branched block ethylene polymers which comprise Nylon
6 grafted via maleic anhydride to a homogeneous ethylene polymer

5   represented by XU58300, an ethylene polymer available from The Dow
Chemical Company. Figure 16 shows the effect of oil on tan delta of
branched block ethylene polymers which comprise Nylon 6 grafted via
maleic anhydride to a homogeneous ethylene polymer represented by
XU58300, an ethylene polymer available from The Dow Chemical Company.

10   Figure 17 compares various branched block ethylene polymers which
comprise various reactive thermoplastic polymers, i.e., PPO/HIPS
(polyphenylene oxide/high impact polystyrene), PCTG, PET and Nylon 6,
grafted via maleic anhydride to MAHg8200. Figure 18 shows the shore A
hardness at various temperatures, as achieved by branched block

15   ethylene polymers which comprise 70 weight percent MAHg8200 and 30
weight percent Nylon 6.

Figure 19 is a plot of viscosity in relation to frequency of
rotation determined by rheometric (dynamic) mechanical spectroscopy at

20   230°C for compositions containing by weight 75% polypropylene and 0,
10, 15, 20, 25 and 30% branched block ethylene polymer.

Figure 20 is a plot of tan delta in relation to frequency of
rotation determined by rheometric (dynamic) mechanical spectroscopy at

25   230°C for compositions containing by weight 75% polypropylene and 0,
10, 15, 20, 25 and 30% branched block ethylene polymer.

In the Figures ITP is a substantially linear ethylene polymer;
PBT is polybutyleneterephthalate; MAH is maleic anhydride; MMA/GMS is

30   methacrylate-butylacrylate-glycidyl methacrylate, 98:8:2 ratio by
weight as further explained in the examples of the invention. DMS is
dynamic mechanical spectrometry; RMS is rheolometric mechanical
spectrometry. The acronym POE is also used for polyolefin elastomer
in the figures for the homogeneous ethylene polymer. RSA is

35   Rheometrics Solids Analyzer

block ethylene polymers of the invention designated with triangles compared with controls which are not examples of the invention. Figure 3 shows the tan delta, E' and E'' of a branched block ethylene polymer of the invention. Figure 4 shows the RMS rheology data at 190

5   ° C of a branched block ethylene polymer of the invention designated by diamonds compared with controls which are not examples of the invention. Figure 5 shows the tan delta at 190° C of a branched block ethylene polymer of the invention designated by diamonds compared with controls which are not examples of the invention. Figure 6 shows the

10   RMS Rheology data at 190° C of branched block ethylene polymers of the invention having different ratios of homogeneous ethylene polymer grafted to maleic anhydride to a reactive thermoplastic polymer represented by nylon. Figure 7 shows the RMS Rheology data at 230° C of branched block ethylene polymers of the invention having different

15   ratios of homogeneous ethylene polymer grafted to maleic anhydride to a reactive thermoplastic polymer represented by nylon. Figure 8 shows the tan delta at 190° C of branched block ethylene polymers of the invention having different ratios of homogeneous ethylene polymer grafted to maleic anhydride to a reactive thermoplastic polymer

20   represented by nylon. Figure 9 shows the tan delta at 230° C of branched block ethylene polymers of the invention having different ratios of homogeneous ethylene polymer grafted to maleic anhydride to a reactive thermoplastic polymer represented by nylon.

25   Figure 10 compares the RMS data at 190° C for a homogeneous ethylene polymer grafted with maleic anhydride (designated MAHg8200 where 8200 is the designation of the ethylene polymer, Engage™ 8200) (not an example of the invention) with branched block ethylene polymers formed by reacting that grafted polymer with PCTG (poly

30   cylclohexanoldimethol terephthalate glycol), PET (polyethylene terephthalate) and Nylon 6. Figure 11 shows the RMS data at 190° C of MAHg8200 (as described above) with branched block ethylene polymers formed by reacting that grafted polymer with Nylon 6, Nylon 11, and Nylon 12. Figure 12 shows the same comparison as Figure 11, but at

35   230° C. Figure 13 shows how the rheology index is improved by the addition of various percentages of Nylon 6 to MAHg8200. Figure 14

reactive thermoplastic polymer capable of reacting with the
ethylenically unsaturated functionalized organic compound. The
ethylene polymer may be considered to be a first polymer block. The
ethylenically unsaturated functionalized organic compound adds to the
5   ethylene polymer through its double bond to form a branched ethylene
polymer. If the branch formed by the ethylenically unsaturated
functionalized organic compound is of sufficient length (containing,
for example, three or more molecules), it may be said to form a second
block itself. However, the branch may be formed by just a single
10   molecule of the ethylenically unsaturated functionalized organic
compound. Regardless of the length of the branch formed by the
ethylenically unsaturated functionalized organic compound, the
branched ethylene polymer reacts, through the functionality on the
residue of the ethylenically unsaturated functionalized organic
15   compound, with the reactive thermoplastic polymer, to form the final
polymer block.

         The branch point, which contains the residue of one or more
molecules of the ethylenically unsaturated functionalized organic
20   compound and allows the bonding of the reactive thermoplastic polymer
as the final polymer block, may be distinguished from long- and short-
chain branching which may occur on an ethylene polymer during its
formation from ethylene and (optionally) another monomer(s) such as an
alpha-olefin. The branch point formed from an ethylenically
25   unsaturated functionalized organic compound, in contrast to branches
formed in conjunction with backbone growth during the polymerization
of ethylene, is added to an ethylene polymer after its original
polymerization to provide the necessary reactive site for bonding of
the reactive thermoplastic polymer as the final polymer block of the
30   branched block ethylene polymer.

Concerning Subcomponent (a) - The Ethylene Polymer

         Subcomponent (a) is an ethylene polymer which forms the
35   first block in the preparation of the branched block ethylene
polymers of the invention. An ethylene polymer useful for such
purpose may include, among others, conventional ethylene polymers

The compositions of this invention are useful, in any
application for which impact modified polymers are used. For example,
they are useful in the production of films, fibers, coatings, extruded
sheets, multi-layer laminates and molded or shaped articles of
5   virtually all varieties, especially profile extruded gaskets, blow
molded or thermoformed articles, automotive fascia, body side moldings
and interior components, and other parts and components for use in the
automotive, electrical and electronics industries. The compositions
of this invention are also useful as hot melt adhesives. The methods
10   of this invention are useful for preparing polymers, compositions and
molded articles having applications which are the same as or similar
to the foregoing.

Branched block ethylene polymers of the invention are
. 15 surprisingly useful as rheologic modifiers, impact strength modifiers
and melt strength enhancers. Modifier effectiveness is a function of
melt elasticity, dispersibility and compatibility of the branched
block ethylene polymer. The branched block ethylene polymers are
useful in blow molding and thermoforming. They are also
20   advantageously useful in oil extension. Additionally, especially when
the reactive thermoplastic polymer is an amine-functionalized polymer,
such as nylon, the branched block ethylene polymer is useful in
forming non-crosslinked foams which are recyclable. In the case of
branched block ethylene polymers wherein the reactive thermoplastic
25   polymer is a nylon, branched block ethylene polymers which utilize
Nylon 11 as the reactive thermoplastic polymer offer the highest melt
strength, followed by that utilizing Nylon 6, followed by that
utilizing Nylon 12.

30   Detailed Description of the Invention

The branched block ethylene polymers of this invention, are
prepared from (i) an ethylene polymer, preferably a polymer having an
M_w/M_n ratio as defined by gel permeation chromotography of less than
35   about 3.0, and more preferably a homogeneous ethylene polymer; (ii) an
ethylenically unsaturated functionalized organic compound; and (iii) a

pressure conditions. LLDPE can be formed as a slurry in a light
hydrocarbon diluent using a supported chromium catalyst, or it can be
formed as a slurry in hexane using organometal-titanium type
catalysts. It can also be formed in a suitable hydrocarbon in
5   solution at approximately 250°C, or it can be formed in gas phase as
described in Levine, USP 4,011,382, or as described in Jezl, USP
4,129,729.

HDPE homopolymer or copolymers are typically about 94%
10   crystalline and have densities of above about 0.935 g/cm^3, and
particularly from about 0.950 to about 0.970 g/cm^3. HDPE, because of
its much greater crystallinity and density, has a higher melting point
than LDPE - 135°C vs. 115°C. A crystalline HDPE homopolymer has a
regular linearity, and typically forms as it cools into ordered
15   agglomerates referred to as crystallites, from which HDPE obtains an
excellent degree of toughness and shatter-resistant character.
Crystallization is disturbed, and density is correspondingly decreased
in HDPE, if ethylene is copolymerized with an α-olefin, as described
above, or if short-chain branching results from side reactions
20   intrinsic for a particular reaction mechanism. For example, HDPE
prepared with Ziegler transition metal catalysts may have from about
0.5 to 4 short-chain branches, particularly methyl groups, per 1000
carbon atoms. The molecular weight of HDPE usually ranges from 50,000
to 1,000,000 or more. Beyond a certain point, increasing the
25   molecular weight of HDPE actually causes a decrease in density because
of chain entanglement, but the effect is not significant. Most
aspects of the strength of HDPE decrease with decreasing molecular
weight. HDPE may be manufactured in a slurry system wherein high
purity ethylene is fed to a loop reactor which contains a low boiling
30   hydrocarbon used to dissolve the ethylene, and to suspend the catalyst
and polymer particles. Alternatively, HDPE can be made in a gas-phase
process wherein no hydrocarbon diluent is used and a fluidized bed is
used to agitate and suspend the polymer particles. Methods for making
HDPE are more particularly described in Hogan, USP 2,825,721.
35

Concerning the Use of a Homogeneous Ethylene Polymer as
Subcomponent (a). Preferably, subcomponent (a) will be a homogeneous

12

such as low density polyethylene ("LDPE"), linear low density polyethylene ("LLDPE"), and high density polyethylene ("HDPE"). LDPE is typically thought of as that which is made under high pressure conditions and has a density from about 0.915 to about

5   0.935 g/cm³. This low density results from the many zones of amorphous arrangement which are characteristic of LDPE because of its long-chain branches, many of which are as long as the backbone. Inasmuch as the density of purely amorphous polyethylene is 0.855 g/cm³, as compared to purely crystalline

10   polyethylene which has a density of 0.97 g/cm³, it can be seen that LDPE does have some crystallinity. However its long-chain branching is its dominant feature. LDPE typically has from 4 to 25 and sometimes as many as 90 of such long-chain branches per 1000 carbon atoms. It also has 10-35 short chains per 1000

15   carbon atoms, containing 2-8 carbon atoms each, which result from backbiting and molecular rearrangement along the backbone during chain growth, rather than from comonomer incorporation as is the case for LLDPE.

20   LDPE can be made in either a tubular reactor or a stirred autoclave, where heated, pressurized feed streams of ethylene gas, free-radical initiator and optional chain transfer agent are injected into the reaction device. The reaction of formation usually occurs at 1,500-3,000 atm (152-304 MPa) and at a

25   temperature usually not exceeding 300°C, as known in the art. During the polymerization of LDPE, ethylene can be copolymerized with other monomers such as vinyl acetate, ethyl acrylate, acrylic acid, vinyl chloride or carbon monoxide.

30   LLDPE is formed under the kind of low pressure conditions which are usually thought of as appropriate for forming HDPE. However, a low density product (0.910 - 0.940 g/cm³) results because, rather than forming a homopolymer, ethylene is copolymerized with one or more α-olefins, which in the final product take on the form and function of

35   short side chains. Because the comonomers most frequently used are α-olefins such as 1-butene, 4-methyl-1-pentene, 1-hexene or 1-octene, these side chains prevent the close, fully crystalline type of packing representative of HDPE, but they are not nearly as long as the fully branched, long side chains associated with LDPE made under high

11

The polydispersity (M_w/M_n) for the homogeneous ethylene polymers
described herein is less than about 3.0, is preferably from about 1.5
to about 2.5, and is more preferably from about 1.7 to about 2.3, and
is most preferably about 2.

5

When they are an ethylene/α-olefin interpolymer, the homogeneous
ethylene polymers will have a homogeneous branching distribution. The
terms "homogeneously branched" and "homogeneous branching
distribution" refer to the fact that (1) the α-olefin comonomer(s)
10 is/are randomly distributed within a given molecule of an
ethylene/comonomer copolymer; (2) substantially all of the copolymer
molecules have the same ethylene/comonomer ratio; (3) the polymer is
characterized by a narrow short chain branching distribution; (4) the
polymer essentially lacks a measurable high density, crystalline
15 polymer fraction [as measured, for example, by techniques such as
those involving polymer fractional elutions as a function of
temperature]; and (5) the polymer is characterized, as determined from
the conditions described in 21 C.F.R. 177.1520(c) and (d), as having
(i) substantially reduced levels of n-hexane extractables (for
20 example, less than 1% extractables for an ethylene/1-octene copolymer
at densities greater than about 0.90 g/cc), or (ii) substantial
amorphism, which is indicated when greater than 75 wt% of the polymer
is soluble under the specified conditions (for example, ethylene/1-
octene copolymer is 90% soluble at a density of about 0.90 g/cm^3, and
25 is 100% is soluble at a density of about 0.88 g/cm^3).

Typically, the homogeneous ethylene polymers have a homogeneous
short chain branching distribution and do not have any measurable high
density fraction, i.e., these polymers do not contain any polymer
30 fraction that has a degree of branching less than or equal to 2
methyls/1000 carbons, as measured by Temperature Rising Elution
Fractionation which is described in USP 5,089,321.

The homogeneity or narrowness of the branching distribution is
35 further indicated by the value of the Composition Distribution Branch
Index ("CDBI") or the Short Chain Branch Distribution Index ("SCBDI").

14

ethylene polymer. Homogeneous polymers are characterized as having a
narrow polydispersity (M_w/M_n) and a homogeneous short chain branching
distribution. The polydispersity (M_w/M_n) of the homogeneous ethylene
polymers described herein may be determined from data generated by gel
5   permeation chromatography (GPC). An instrument typically used for
this purpose is a Waters 150°C high temperature chromatographic unit
equipped with three mixed porosity bed columns (Polymer Laboratories
103, 104, 105 and 106), operating at a system temperature of 140°C.
The solvent used is 1,2,4-trichlorobenzene, from which 0.3 weight
10 percent solutions of the samples are prepared for injection. The flow
rate is 1.0 milliliter/minute, and the injection size is 200
microliters.

Molecular weight determination for polyethylene is made by using
15 narrow molecular weight distribution polystyrene standards (from
Polymer Laboratories) in conjunction with their elution volumes. The
equivalent polyethylene molecular weights are determined by using
appropriate Mark-Houwink coefficients for polyethylene and
polystyrene, as described by Williams and Word in *Journal of Polymer*
20 *Science*, Polymer Letters, volume 6, page 621, 1968 (incorporated
herein by reference), to derive the following equation:

$$M_{polyethylene} = a * (M_{polystyrene})^b$$

25 in which a = 0.4316, b = 1.0, and M is molecular weight for
polyethylene and polystyrene in 1,2,4-trichlorobenzene. Weight
average molecular weight, M_w, is calculated in the usual manner
according to the following formula: $M_w = \sum w_i * M_i$, where w_i and M_i are
the weight fraction and molecular weight, respectively, of the ith
30 fraction eluting from the GPC column. Number average molecular
weight, M_n, is calculated in the usual manner according to the
following formula: $M_n = [\sum n_i * M_i]/\sum n_i$, where n_i and M_i are,
respectively, the number of molecules in, and the molecular weight of,
the ith fraction eluting from the GPC column. The symbol * indicates
35 a step of multiplication.

27°C, and more typically within 20°C of the melting point of the single melting peak.

5   The single melting peak is determined using a differential scanning calorimeter standardized with indium and deionized water. The method involves about 5 samples of 7 mg size, a "first heat" to about 150°C which is held for 4 minutes, a cool down at 10°C/min to 30°C which is held for 3 minutes, and a heat up at 10°C/min to 150°C for the "second heat" heat flow versus temperature curve. Total heat

10   of fusion of the polymer is calculated from the area under the curve. The heat of fusion attributable to the artifact described above, if present, can be determined using an analytical balance and weight percent calculations.

15   One known class of homogeneous ethylene polymers are "homogeneous linear ethylene polymers." Homogeneous ethylene polymers have no long-chain branching, as defined below. The term "linear" does not refer to bulk high pressure branched polyethylene, ethylene/vinyl acetate copolymers, or ethylene/vinyl alcohol

20   copolymers inasmuch as these kinds of polymers are known to those skilled in the art to have numerous long chain branches.

       Homogeneous linear ethylene polymers are from a known class of polymers, examples of which include those described in USP 3,645,992

25   (Elston), those made using so called single site catalysts in a batch reactor having relatively high ethylene concentrations [as described in U.S. Patent 5,026,798 (Canich) or in U.S. Patent 5,055,438 (Canich)], and those made using constrained geometry catalysts in a batch reactor also having relatively high olefin concentrations [as

30   described in U.S. Patent 5,064,802 (Stevens) or in EP-A-416 815 (Stevens)]. These polymers have an absence of long chain branching, as described by Van der Sanden and Halle in *Tappi Journal*, February 1992. Processes using metallocene catalysts to produce homogeneous linear ethylene polymers have been developed, as shown, for example,

35   in Ewen, USP 4,937,299, EP 129,368, EP 260,999, USP 4,701,432, USP 4,937,301, USP 4,935,397, USP 5,055,438 and WO 90/07526, each of which

CDBI is defined as the weight percent of the polymer molecules having

a comonomer content within 50 percent of the median total molar

comonomer content. The CDBI of a polymer is readily calculated, for

example, by employing temperature rising elution fractionation, as

5   described in Wild, *Journal of Polymer Science*, Polymer Physics

Edition, Volume 20, page 441 (1982), or in U.S. Patent 4,798,081. The

CDBI for the homogeneous ethylene/α-olefin interpolymers used in the

present invention is greater than about 30 percent, is preferably

greater than about 50 percent, is more preferably greater than about

10   80 percent, and is most preferably greater than about 90 percent.

Homogeneous ethylene polymers do not include, by definition,

heterogeneously branched linear low density polyethylenes or linear

high density polyethylenes made using Ziegler-Natta polymerization

15   processes (as described, for example, in Anderson, USP 4,076,698); or

the branched high pressure, free-radical polyethylenes and other high

pressure ethylene copolymers (e.g., ethylene/vinyl acetate or

ethylene/vinyl alcohol copolymers), which are known to those skilled

in the art to have numerous long chain branches.

20

To the extent that the homogeneous ethylene polymer in an

ethylene/α-olefin interpolymer, it will have only a single melting

peak, as measured by differential scanning calorimetry (DSC) between -

30°C and 150°C. This is in contrast to Ziegler-polymerized,

25   heterogeneously branched linear ethylene polymers, which have 2 or

more melting peaks because of their broad branching distribution.

However, for certain classes of homogeneous ethylene polymers having a

density of about 0.875 g/cm^3 and about 0.91 g/cm^3, the single melt

peak may show, depending on equipment sensitivity, a "shoulder" or a

30   "hump" on the low side of the melting peak (i.e. below the melting

point) that constitutes less than 12 percent, typically, less than 9

percent, more typically less than 6 percent of the total heat of

fusion of the polymer. This artifact is due to intrapolymer chain

variations, and it is discerned on the basis of the slope of the

35   single melting peak varying monotonically through the melting region

of the artifact. Such artifact occurs within 34°C, typically within

15

herein, the onset of surface melt fracture is characterized as the
beginning of losing extrudate gloss at which the surface roughness of
extrudate can only be detected by 40x magnification. Substantially
linear ethylene polymers will further be characterized by a critical
5   shear rate at the onset of surface melt fracture which is at least 50
percent greater than the critical shear rate at the onset of surface
melt fracture of a linear olefin polymer having about the same I_2 and
M_w/M_n. An apparent shear stress versus apparent shear rate plot is used
to identify the melt fracture phenomena over a range of nitrogen
10   pressures from 5250 to 500 psig using the die or gas extrusion
rheometer (GER) test apparatus as described by Shida et al in *Polymer
Engineering Science*, Volume 17, No. 11 (1977), page 770, and in
Rheometers for Molten Plastics by John Dealy, Van Nostrand Reinhold
Co. (1982), pages 97-99. According to Ramamurthy in *Journal of*
15   *Rheology*, 30(2), 337-357 (1986), above a certain critical flow rate,
the observed extrudate irregularities may be broadly classified into
two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow
20   conditions, and ranges in detail from loss of specular gloss to the
more severe form of "sharkskin". In this disclosure, the onset of
surface melt fracture is characterized as the beginning of the loss of
extrudate gloss, at which the surface roughness of extrudate can only
be detected by 40X magnification. The critical shear rate at onset of
25   surface melt fracture for a substantially linear ethylene polymer is
at least 50 percent greater than the critical shear rate at the onset
of surface melt fracture for a conventional linear ethylene polymer as
to which the I_2, polydispersity and density is each within 90-110
percent of the corresponding value for the substantially linear
30   ethylene polymer. Preferably, the critical shear stress at the onset
of surface melt fracture for the substantially linear ethylene
polymers is greater than about 2.8×10^6 dynes/cm^2.

Gross melt fracture occurs at unsteady flow conditions, and
35   ranges in detail from regular surface distortions (such as alternating
roughness and smoothness, or helical patterns) to random distortions.

is incorporated herein by reference. Such polymers can be made by
conventional polymerization processes such as gas phase, slurry or
solution.

5   A preferred, known class of homogeneous ethylene polymers are
"substantially linear ethylene polymers", and are characterized by a
desirable level of processability, e.g. low susceptibility to melt
fracture, even under high shear stress conditions. Substantially
linear ethylene polymers have a critical shear rate at the onset of
10   surface melt fracture which is substantially higher than, and a
processing index which is substantially lower than, that of a linear
polyethylene at the same molecular weight distribution and melt index.
Substantially linear ethylene polymers have a shear thinning and ease
of processability similar to highly branched low density polyethylene
15   (LDPE), but also have the strength and toughness of linear low density
polyethylene (LLDPE). The substantially linear ethylene polymers
described herein, and processes for making same, are also described in
USP 5,272,236, USP 5,278,272 and U.S. SN 08/301,948.

20   As used herein, "substantially linear ethylene polymer" means
that, in addition to the short chain branches attributable to any
comonomer incorporation, the polymer is further characterized as
having long chain branches. Substantially linear ethylene polymers
are characterized as having a melt flow ratio I_{10}/I_2 which is greater
25   than or equal to 5.63, a molecular weight distribution (as determined
by gel permeation chromatography) M_w/M_n which is less than or equal to
$I_{10}/I_2-4.63$, and a critical shear rate at the onset of surface melt
fracture at least 50 percent greater than a linear ethylene polymer
having essentially the same I_2 and M_w/M_n and/or a critical shear stress
30   at the onset of surface melt fracture of greater than about 2.8×10^6
dynes/cm^2.

          According to Ramamurthy in *Journal of Rheology*, 30(2), 337-357,
1986, above a certain critical flow rate, surface melt fracture may
35   occur, which may result in irregularities ranging from loss of
specular gloss to the more severe form of "sharkskin". As used

where 2.15×10^6 dyne/cm^2 is the shear stress at 2500 psi, and the shear rate is the shear rate at the wall as represented by the following equation:

5
$$\frac{32Q'}{(60 \text{ sec/min})(0.745)(\text{diameter} \times 2.54 \text{ cm/in})^3}$$

where: Q' is the extrusion rate in g/min, 0.745 is the melt density of polyethylene in g/cm^3, and diameter is the orifice diameter of the 10 capillary in inches. The PI is the apparent viscosity of a material measured at an apparent shear stress of 2.15×10^6 dynes/cm^2.

For a substantially linear ethylene polymer, the PI is less than or equal to 70 percent of that of a conventional linear ethylene 15 polymer as to which the I_2, M_w/M_n and density is each within 90-110 percent of the corresponding value for the substantially linear ethylene polymer.

Substantially linear ethylene polymers further have an improved 20 melt elasticity or melt tension as compared to homogeneous linear ethylene polymers. "Melt tension" is measured by a specially designed pulley transducer in conjunction with a melt indexer. Melt tension is the load exerted by the extrudate or filament while passing over the pulley onto a two inch drum rotating at the standard speed of 30 rpm. 25 The melt tension measurement is similar to that performed by the "Melt Tension Tester" made by Toyoseiki, and is described by John Dealy in *Rheometers for Molten Plastics*, Van Nostrand Reinhold Co. (1982), pages 250-251. The melt tension of the substantially linear ethylene polymers described herein is at least about 2 grams, and, particularly 30 with respect to those having a narrow molecular weight distribution such as about 1.5 to 2.5, the melt tension is typically at least about 5 percent, and can be as much as about 60 percent, greater than the melt tension of a conventional linear ethylene interpolymer as to which the melt index, polydispersity and density is each within 90-110 35 percent of the corresponding value for the substantially linear ethylene polymer.

20

For commercial acceptability (e.g. in blown film products), surface
defects should be minimal, if not absent. The critical shear rate at
onset of surface melt fracture (OSMF), and the critical shear stress
at onset of gross melt fracture (OGMF), are related herein to the

5   changes of surface roughness and configurations of the extrudate
produced by a GER. For the substantially linear ethylene polymers
described herein, the critical shear stress at onset of gross melt
fracture is preferably greater than about 4 x 10^6 dyne/cm^2.

10   For the GER melt fracture determination and for the processing
index (PI) determination described below, the substantially linear
ethylene polymers are tested without inorganic fillers, and with 20
ppm or less aluminum catalyst residue. For these determinations the
polymer will preferably contain, antioxidants, such as phenols,

. 15   hindered phenols, phosphites or phosphonites, preferably a combination
of a phenol or hindered phenol and a phosphite or a phosphonite.

A further indicator of the improved processability of
substantially linear ethylene polymers is the rheological processing

20   index (PI). The PI is the apparent viscosity (in kpoise) of a
polymer, and is measured by a gas extrusion rheometer (GER). The GER
is described above in conjunction with the determination of melt
fracture phenomena. The processing index is measured at 190°C with a
nitrogen pressure of 2500 psig. For high flow polymers (e.g. polymer

25   having an I_2 of 50 - 100 g/10 min. or greater), a die having a
diameter of 0.0296 inch (752 microns), preferably 0.0143 inch, having
a 20:1 length/diameter ratio, and having an entrance angle of 180° is
used.

30   The processing index is calculated in millipoise units from the
following equation:

$$PI = \frac{2.15 \times 10^6 \ dyne/cm^2}{(1000 \times shear\ rate)}$$

35

polymerization process, although slurry and gas phase polymerization processes are also useful, provided the proper catalysts and polymerization conditions are employed. Multiple reactor polymerization processes are also useful for this purpose, such as

5   those disclosed in USP 3,914,342. The multiple reactors can be operated in series or in parallel, with at least one constrained geometry catalyst employed in at least one of the reactors.

In general, continuous polymerization is advantageously

10   accomplished at conditions known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, for example, temperatures from about 0 to 250°C and pressures from atmospheric to 1000 atmospheres (100 MPa). A support may be employed, but preferably the catalysts are used in a homogeneous (i.e. soluble) manner. It will,

15   of course, be appreciated that the active catalyst system forms in situ if the catalyst, and the cocatalyst components thereof, are added directly to the polymerization process, and a suitable solvent or diluent, including condensed monomer, is used. It is, however, preferred to form the active catalyst in a separate step in a suitable

20   solvent prior to adding same to the polymerization mixture.

Preferably, the term "substantially linear ethylene polymer" designates that the bulk polymer is substituted, on average, with about 0.01 long-chain branch/1000 total carbon atoms (including both

25   backbone and branch carbons) to about 3 long-chain branches/1000 total carbons. Preferred polymers are substituted with about 0.01 long-chain branch/1000 total carbons to about 1 long-chain branch/1000 total carbons, more preferably from about 0.05 long-chain branch/1000 total carbons to about 1 long-chain branch/1000 total carbons, and

30   especially from about 0.3 long-chain branch/1000 total carbons to about 1 long-chain branch/1000 total carbons.

As used herein, the term "backbone" refers to a discrete molecule, and the term "polymer" or "bulk polymer" refers in the

35   conventional sense to the polymer as formed in a reactor. The term "bulk" polymer means the polymer which results from the polymerization

22

A further unique characteristic of these substantially linear
ethylene polymers is a flow property which causes the I_{10}/I_2 value to
be essentially independent of polydispersity (M_w/M_n). This is a
5   significant difference from conventional Ziegler-polymerized
heterogeneous polyethylene resins, and from conventional single-site-
catalyst-polymerized homogeneous polyethylene resins, the rheological
properties of which are such that as polydispersity (M_w/M_n) increases,
the I_{10}/I_2 value also increases. It should be noted that peroxide need
10   not be added to the substantially linear ethylene polymers in order
for the polymers to exhibit an I_{10}/I_2 independent of polydispersity
(M_w/M_n) and the melt fracture properties.

Generally, the I_{10}/I_2 ratio of the substantially linear ethylene
15   polymers is at least about 5.63, is preferably at least about 7, is
especially at least about 8, and is most preferably at least about 9
or above. The only limitation on the maximum I_{10}/I_2 ratio are
practical considerations such as economics or polymerization kinetics,
but typically the maximum I_{10}/I_2 ratio does not exceed about 20, and
20   preferably does not exceed about 15. In contrast, the I_{10}/I_2 ratio of
the homogeneous linear ethylene polymers described herein is generally
6 or less.

The advantageous melt elasticity and processibility of
25   substantially linear ethylene polymers result, it is believed, from
their method of production. The polymers may be produced via a
continuous (as opposed to a batch) controlled polymerization process
using at least one reactor, for example as disclosed in WO 93/07187,
WO 93/07188 or WO 93/07189. However, these polymers can also be
30   produced using multiple reactors, using for example a multiple reactor
configuration as described in USP 3,914,342 at a polymerization
temperature and pressure sufficient to produce the interpolymers
having the desired properties.

35   The polymerization conditions for manufacturing substantially
linear ethylene polymers are generally those useful in a solution

21

Long-chain branching can be distinguished from short-chain branching by using ^{13}C nuclear magnetic resonance spectroscopy (NMR), and, for ethylene homopolymers and for copolymers of ethylene and a C_2-C_6 α-olefin , it can be quantified using the method of Randall in

5   *Journal of Macromolecular Science-Reviews in Macromolecular Chemistry and Physics*, Volume C29, pages 285-297 (1989). However, as a practical matter, the portion of a long-chain branch beyond the sixth carbon atom cannot be distinguished using current ^{13}C NMR for the purpose of determining the precise length of the long-chain branch

10 and, as such, this analytical technique cannot distinguish between a seven (7) carbon branch and a seventy (70) carbon branch.

USP 4,500,648, incorporated herein by reference, teaches that long-chain branching frequency (LCBF) can be represented by the

15 equation LCBF = b/Mw where b is the weight average number of long-chain branches per molecule, and Mw is the weight average molecular weight. The molecular weight averages and the long-chain branching characteristics are determined by gel permeation chromatography and intrinsic viscosity methods.

20

Other known techniques useful for determining the presence of long chain branches in ethylene polymers, including ethylene/1-octene interpolymers. Two such methods are gel permeation chromatography coupled with a low angle laser light scattering detector (GPC-LALLS)

25 and gel permeation chromatography coupled with a differential viscometer detector (GPC-DV). The use of these techniques for long chain branch detection and the underlying theories have been well documented in the literature. See, e.g., Zimm, G.H. and Stockmayer, W.H., J. Chem. Phys., 17, 1301 (1949) and Rudin, A., Modern Methods of

30 Polymer Characterization, John Wiley & Sons, New York (1991) pp. 103-112.

A. Willem deGroot and P. Steve Chum, both of The Dow Chemical Company, at the October 4, 1994 conference of the Federation of

35 Analytical Chemistry and Spectroscopy Society (FACSS) in St. Louis, Missouri, presented data demonstrating that GPC-DV is a useful

24

process and, for these substantially linear ethylene polymers, includes molecules having both an absence of long-chain branching, as well as molecules which do have long-chain branching. Thus a "bulk" polymer includes all molecules formed during polymerization. It is

5   understood that, for the substantially linear ethylene polymers, not all molecules have long-chain branching, but a sufficient number of same do such that the average long-chain branching content of the bulk polymer advantageously affects the melt rheology (i.e. the melt fracture properties) of the bulk polymer. For the polymer to be a

10 "substantially linear" ethylene polymer, the polymer must have at least enough molecules with long-chain branching such that the average long-chain branching in the bulk polymer is at least an average of about 0.01/1000 total carbons.

- 15   When a substantially linear ethylene polymer, which contains long-chain branching, is an ethylene/α-olefin interpolymer, the long-chain branch may have a chain length of at least one (1) carbon less than the number of carbons in the comonomer. A short-chain branch, by contrast, is defined as having a chain length of the same number of

20 carbons in the residue of the comonomer after it is incorporated into the polymer molecule backbone. For example, an ethylene/1-octene substantially linear ethylene polymer has a backbone with long-chain branches of at least seven (7) carbons in length, but it also has short chain branches of only six (6) carbons in length.

25

For ethylene/alpha-olefin interpolymers, the long chain branch is longer than the short chain branch that results from the incorporation of the alpha-olefin(s) into the polymer backbone. The empirical effect of the presence of long chain branching in the

30 substantial linear ethylene/alpha-olefin interpolymers used in the invention is manifested as enhanced rheological properties which are quantified and expressed herein in terms of gas extrusion rheometry (GER) results and/or melt flow, I_{10}/I_2, increases, as is described above.

35

23

"Substantially linear ethylene polymers" are prepared by using
constrained geometry catalysts, and are characterized by a narrow
polydispersity (molecular weight distribution) and by a narrow
comonomer distribution. As herein used, "interpolymer" means a
5   polymer of two or more comonomers, e.g., a copolymer, terpolymer,
etc., or in other words, a polymer made by polymerizing ethylene with
at least one other comonomer. Other basic characteristics of these
substantially linear ethylene polymers include a low residuals content
(i.e., low concentrations in the substantially linear ethylene polymer
10   of the catalyst used to prepare the polymer, unreacted comonomers, and
low molecular weight oligomers made during the course of the
polymerization), and a controlled molecular architecture which
provides good processability even though the molecular weight
distribution is narrow relative to conventional olefin polymers.
15
Although it is preferred to use a substantially linear
ethylene polymer for preparation of the branched block ethylene
polymers, a combination of any two or more of the different kinds
of ethylene polymers described above may be used as well. The
20   differences in the various kinds of ethylene polymers may be
illustrated by the use, for example, of (i) a conventional LLDPE
together with a substantially linear ethylene polymer, or (ii) a
substantially linear ethylene homopolymer together with a
substantially linear ethylene/α-olefin interpolymer, (iii) two or
25   more substantially linear ethylene polymers made with different
constrained geometry catalysts, (iv) two or more substantially
linear ethylene polymers made in different reactors or reaction
zones, or (v) two or more substantially linear ethylene polymers
having different properties such as density, M_w/M_n, I_2 or I_{10}/I_2.
30   The differences among the ethylene polymers contained in such a
combination may manifest themselves in the form, for example, of
multi-modal densities, a broadened M_w/M_n, and/or multiple melting
peaks. Such a combination of ethylene polymers, if employed, may
be advantageously prepared using the dual reaction polymerization
35   process described below.

General Properties of the Ethylene Polymer:

26

technique for quantifying the presence of long chain branches in substantially linear ethylene interpolymers. In particular, deGroot and Chum found that the level of long chain branches in substantially linear ethylene homopolymer samples measured using the Zimm-Stockmayer

5   equation correlated well with the level of long chain branches measured using ^{13}C NMR.

Further, deGroot and Chum found that the presence of octene does not change the hydrodynamic volume of the polyethylene samples in

10   solution and, as such, one can account for the molecular weight increase attributable to octene short chain branches by knowing the mole percent octene in the sample. By deconvoluting the contribution to molecular weight increase attributable to 1-octene short chain branches, deGroot and Chum showed that GPC-DV may be used to quantify

- 15   the level of long chain branches in substantially linear ethylene/octene copolymers.

deGroot and Chum also showed that a plot of Log(I_2, Melt Index) as a function of Log(GPC Weight Average Molecular Weight) as

20   determined by GPC-DV illustrates that the long chain branching aspects (but not the extent of long branching) of substantially linear ethylene polymers are comparable to that of high pressure, highly branched low density polyethylene (LDPE) and are clearly distinct from ethylene polymers produced using Ziegler-type catalysts such as

25   titanium complexes and ordinary homogeneous catalysts such as hafnium and vanadium complexes.

In contrast to the term "substantially linear ethylene polymer", the term "linear" means that the polymer lacks measurable or

30   demonstrable long chain branches, i.e., the polymer is substituted with an average of less than 0.01 long branch/1000 carbons, with long chain branching being defined herein as a chain length of at least 6 carbons, above which the length cannot be distinguished using ^{13}C nuclear magnetic resonance spectroscopy.

35

The molecular weight of the ethylene polymer is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190°C/2.16 kg [formerly known as "Condition (E)" and also known as I_2]. Melt index value is
5   inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. The I_2 melt index for the ethylene polymer will be generally about 0.01 grams/10 minutes ("g/10 min") or more, preferably about 0.1 g/10 min or more, more
10   preferably about 0.5 g/10 min or more, and most preferably about 1.0 g/10 min or more. The I_2 melt index for the ethylene polymer will be generally about 1000 g/10 min or less, preferably about 500 g/10 min or less, more preferably about 250 g/10 min or less, and most preferably about 100 g/10 min or less.

·15

The Use of Dual Reactor Systems to Prepare the Ethylene Polymer:
Multiple reactor polymerization processes, such as those disclosed in USP 3,914,342, U.S. SN 08/010,958 (filed January 29, 1993) and U.S. SN 08/208,068 (filed March 8, 1994), in which the multiple reactors can
20   be operated in series or in parallel, are often advantageous in preparing ethylene polymers. When the reactors are run in parallel, the polymerization product of each, while still in solution, is combined together in one mixture. When multiple reactors are run in series, the product of a first reactor or reaction zone is passed into
25   a second reactor or reaction zone, wherein further monomer and catalyst are added.

To the extent that little if any live catalyst is passed from a first reactor or zone into a second reactor or zone, the product
30   emerging from a second reactor or zone is predominantly, if not completely, a combination of the individual polymers prepared separately in each reactor or zone, just as when the reactors are run in parallel. However, the ethylene polymers described herein are considered to include the resulting product should it happen that
35   monomer is polymerized onto the same polymer chain in both a first and second reactor or zone.

After the product streams from parallel reactors are combined, or after product emerges from the final reactor or zone in a series,

28

        The ethylene polymer may be an ethylene homopolymer, or may be
an interpolymer of ethylene and one or more C_3-C_{20} α-olefin comonomers
and/or one or more C_4-C_{12} diolefins. The ethylene polymer can also be
an interpolymer of ethylene with at least one of the above C_3-C_{20}
5   alpha olefins and/or diolefins in combination with other unsaturated
monomers. Frequently, the ethylene polymer will be an interpolymer of
ethylene with just one C_3-C_{20} α-olefin, and are more preferably will
be an interpolymer of ethylene with propene, isobutylene, 1-butene, 1-
hexene, 4-methyl-1-pentene or 1-octene, with an interpolymer of
10   ethylene and 1-octene being especially preferred. Other preferred
monomers for interpolymerization include styrene, halo or alkyl
substituted styrenes, vinylbenzocyclobutene, 1,4 hexadiene, and
naphthenics (e.g. cyclopentene, cyclohexene and cyclooctene).

- 15   Preferred ethylene polymers will comprise from 50 to 95 weight
percent ethylene and from 5 to 50, and preferably from 10 to 25,
weight percent of at least one comonomer. Comonomer content is
measured using infrared spectroscopy according to ASTM D-2238, Method
B.
20

        The density of the ethylene polymer is measured in accordance
with ASTM D-792, and is generally at least about 0.85 g/cm^3, is
frequently at least about 0.865 g/cm^3, and is occasionally at least
about 0.89 g/cm^3. The density of the ethylene polymer is generally
25   0.96 g/cm^3 or less, is frequently 0.93 g/cm^3 or less, and is
occasionally 0.90 g/cm^3 or less. The density measurement is often
made of the polymer neat, i.e. a polymer without inorganic fillers and
not containing in excess of 20 ppm aluminum from catalyst residue.

30   In certain instances, the ethylene polymers described herein are
crystalline and/or semi-crystalline polymers. They are normally solid
at room temperature, and are pelletizable at ambient conditions or at
temperatures induced by cooled water. For example, a substantially
linear ethylene/1-octene copolymer having a density of 0.865 g/cm^3 has
35   about 10% crystallinity at room temperature.

is the preferred ethylenically unsaturated organic compound containing at least one carbonyl group.

Ethylenically Unsaturated Functionalized Organic Compounds

5   Containing at Least One Epoxy Ring. Representative examples of ethylenically unsaturated organic compounds containing at least one epoxy ring include, for example, glycidyl esters of unsaturated carboxylic acids (e.g. glycidyl methacrylate); glycidyl ethers of unsaturated alcohols (e.g. allyl-glycidyl-ether) and of alkenylpheno

10 ls (e.g. isopropenylphenyl-glycidylether); and vinyl and allyl esters of epoxycarboxylic acids (e.g. vinyl esters of epoxidized oleic acid). Other ethylenically unsaturated organic compounds containing at least one epoxy ring are described in Laughner, US-A-5,369,154, which is incorporated herein. Of these, glycidyl methacrylate is preferred.

15

Ethylenically Unsaturated Functionalized Organic Compounds

Containing at Least One Amine Functionality. Representative of the amines are amine compounds having at least one ethylenically unsaturated group, for instance, allyl amine, propenyl amine, butenyl

20 amine, pentenyl amine, hexenyl amine; amine ethers including isopropenylphenyl ethyl amine ether and its homologues (branched, cyclic and unbranched), vinyl and allyl ethers of amine compounds, vinyl and allyl esters of amine substituted acids and the like. In each case, the amine and unsaturation are in any position in which

25 they do not undesirably interfere with the graft reactions. Additionally, the amines are unsubstituted or optionally substituted with any groups such as alkyl groups (preferably of from about 1 to about 20 carbon atoms), aryl groups (preferably of from about 6 to about 30 carbon atoms), halogen, ether, thioether groups and the like

30 which do not undesirably interfere with the grafting reactions.

Ethylenically Unsaturated Organic Compounds Containing at Least

One Alcohol Functionality. Representative of the alcohols are any compound, having a hydroxyl group and at least one ethylenically

35 unsaturated group, for instance allyl and vinyl ethers of alcohol compounds like ethyl alcohol and its homologues (branched cyclic and

any solvent is removed, as is known in the art, to recover all the
polymer together as one product.

5   The various reactors or zones which are run in series or
parallel may differ with respect to features such as the type of
catalyst used in each, the type of α-olefin comonomer fed to each, or
the temperature at which each is run. For example, a constrained
geometry catalyst could be used in one reactor or zone and a Ziegler
catalyst could be used in another. When reactors are run in parallel,
10   the combined stream or effluent from which the final product is
recovered need not contain an equal portion of the output of each
reactor.

Concerning Subcomponent (b), The Ethylenically Unsaturated
15   Functionalized Organic Compound:

        Subcomponent (b), the ethylenically unsaturated functionalized
organic compound used in the preparation of the branched block
ethylene polymers of this invention, will contain a carbon-carbon
20   double bond, and will form a branch off of a narrow polydispersity
ethylene polymer by, for example, grafting thereto. These
ethylenically unsaturated functionalized organic compounds are
functionalized, containing functional groups, for example, such as a
carbonyl group (-C=O), (e.g. carboxylic acid or anhydride) or an epoxy
25   ring, an amine, or an alcohol, or the ethylenically unsaturated
functionalized organic compound may be an oxazoline.

        Ethylenically Unsaturated Functionalized Organic Compounds
Containing at Least One Carbonyl Group. Representative of such
30   compounds which contain at least one carbonyl group are the
unsaturated carboxylic acids, and their esters, anhydrides and salts
(both metallic and nonmetallic) thereof. Preferably, the organic
compound contains ethylenic unsaturation conjugated with a carbonyl
group. Representative compounds include acrylic, methacrylic, maleic,
35   fumaric, itaconic, crotonic, methyl crotonic and cinnamic acid, and
their ester, anhydride and salt derivatives, if any. Maleic anhydride

29

functionalized ethylenically unsaturated organic compound is
present as a branch point to react with the reactive
thermoplastic polymer of subcomponent (c) to form the branched
block ethylene polymer of the invention.

5

The ethylenically unsaturated functionalized organic compound
can be grafted to the ethylene polymer by any known technique within
the skill in the art, such as those taught in USP 3,236,917 and USP
5,194,509. For example, in the '917 patent the polymer is introduced
10   into a two-roll mixer and mixed at a temperature of 60°C. The
ethylenically unsaturated organic compound is then added along with a
free radical initiator, such as, for example, benzoyl peroxide, and
the components are mixed at 30°C until the grafting is completed. In
the '509 patent, the procedure is similar except that the reaction
15   temperature is higher, e.g., 210 to 300°C, and a free radical
initiator is not used or is used at a reduced concentration.

An alternative and preferred method of grafting is taught in USP
4,950,541, by using a twin-screw devolatilizing extruder as the mixing
20   apparatus. The ethylene polymer and ethylenically unsaturated organic
compound are mixed and reacted within the extruder at temperatures at
which the reactants are molten and in the presence of a free radical
initiator. Preferably, the ethylenically unsaturated organic compound
is injected into a zone maintained under pressure within the extruder.
25

Concerning Subcomponent (c), The Reactive Thermoplastic Polymer:

Subcomponent(c), the reactive thermoplastic polymer utilized in
the preparation of the branched block ethylene polymers of this
30   invention, is suitably produced by the condensation of bifunctional
monomers or other means within the skill in the art.

The reactive thermoplastic polymer is advantageously a
semicrystalline or amorphous polymer containing functional groups that
35   can react with the functionalized ethylene copolymer in a melt mixing
process. Semicrystalline polymers preferably have $T_m > 70°C$. Amorphous

unbranched) as well as vinyl and allyl esters of alcohol substituted,
preferably carboxylic, acids as well as such compounds as propenyl
alcohol, butenyl alcohol, pentenyl alcohol, hexenyl alcohol, heptenyl
alcohol, octenyl alcohol. In each case, the alcohol and unsaturation

5   are in any position in which they do not undesirably interfere with
the graft reactions. Additionally, the alcohols are unsubstituted or
optionally substituted with any groups such as alkyl groups
(preferably of from about 1 to about 20 carbon atoms), aryl groups
(preferably of from about 6 to about 30 carbon atoms), halogen, ether,

10   thioether groups and the like which do not undesirably interfere with
the grafting reactions.

Oxazoline Compounds for Use as the Ethylenically Unsaturated
Functionalized Organic Compound. Representative oxazoline compounds

- 15   for use herein include those of the general formula

$$C(J_2){=}{=}C(J){-}C{=}{=}N{-}C(J_2){-}C(J_2){-}O$$
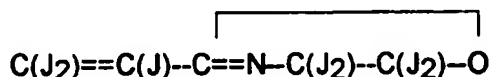
where each J is independently hydrogen, halogen, a C_1-C_{10} alkyl radical

20   or a C_6-C_{14} aryl radical.

The ethylenically unsaturated functionalized organic
compound is used in an amount such that, after addition to the
ethylene polymer to form the branched ethylene polymer, the

25   portion of the branched ethylene polymer derived from the vinyl
compound constitutes by weight, at least about 0.01 percent,
preferably at least about 0.1 percent, and more preferably at
least about 0.2 percent, and yet not more than about 10 percent,
preferably not more than about 5 percent, and more preferably not

30   more than about 2 percent of the ethylenically unsaturated
organic compound.

Non-functionalized vinyl compounds (for example, an
ethylenically unsaturated aromatic compound such as styrene) may

35   be substituted for a portion of the ethylenically unsaturated
functionalized organic compound, provided that enough

31

known as amine-functionalized polymers. One variety of amine-
functionalized polymer is a polyamide, which may be produced by
the condensation of bifunctional monomers, typically those
containing acid and amine functionalities, where the monomers
5   have either the same or different functional groups. For
example, if hexamethylenediamine is reacted with adipic acid, an
-[-AABB-]- type polyamide is obtained wherein the diamine and
diacid units alternate. However, when a monomer such as an amino
acid or a cyclic lactam is self-polymerized, an -[-AB-]- type
10   polyamide results from a regular head-to-tail polymerization,
similar to an addition mechanism. For example, when Nylon-6 is
made, heat is applied to raise the temperature of the caprolactam
to 240-280°C, and catalysts such as water and phosphoric acid are
added to the system. Hydrolysis ensues, the ring opens and
15   polymerization takes place while unreacted monomer is removed
from the system and recycled. Polycondensation and growth of the
polymer chain results from the removal of water from the system.

The polyamides suitable for use herein also include those
20   wherein two or more different diamines, and/or different diacids
and/or different amino acids are polymerized together to form a random
or block co-polyamide. The carbon chain between the functional groups
may be linear or branched aliphatic, alicyclic or aromatic
hydrocarbons. The chains may also contain hetero atoms such as
25   oxygen, sulfur or nitrogen. Also suitable for use herein are block or
random copolymers, such as those resulting, for example, from melt
mixing two or more different polyamides, from reaction of a diamine or
diacid monomer that contains an amide linkage with another diamine or
diacid, or from reaction of a diisocyanate with a dicarboxylic acid.
30
Polyamides are most often prepared by direct amidation in which
the amine group of a diamine or an amino acid bonds to the carboxyl of
a diacid with the accompanying elimination of water. Derivatives of
the acid function, such as an ester, acyl halide or amide, may be used
35   as an alternative source of the carboxyl functionality, in which case
the by-product is an alcohol, a hydrogen halide or ammonia,
respectively. Formation of polyamides can also occur by ring-opening
polymerization of a caprolactam, such as when Nylon-6 is made from a
caprolactam. Suitable polyamides are Nylon-11, Nylon-12, and in
40   general nylon with a crystalline melting point less than 280°C, often

34

polymers preferably have $T_g > 50°C$. Suitable functional groups include hydroxyl, phenolic, amine, epoxy, and isocyanate. Examples of suitable reactive thermoplastic polymers include polybutyleneterephthalate (PBT), polyethyleneterephthalate (PET),

5 Nylon-6, polysulfone, polyurethane, polycarbonate, polymethylmethacrylate functionalized with epoxy, styrene acrylonitrile functionalized with epoxy, or other functional groups, preferably those listed above.

10   Typically, the reactive thermoplastic polymer is used in an amount such that, after addition to the branched ethylene polymer to form a branched ethylene block polymer, the portion of the branched ethylene block polymer derived from the reactive thermoplastic polymer constitutes by weight, at least about 1

15 percent, preferably at least about 2 percent, and more preferably at least about 5 percent, and yet not more than about 40 percent, preferably not more than about 30 percent, and more preferably not more than about 25 percent of the branched block ethylene polymer.

20

        One suitable class of reactive thermoplastic polymers is the class known as engineering thermoplastics. The third edition of the Kirk-Othmer Encyclopedia of Science and Technology defines engineering plastics as thermoplastic resins, neat or unreinforced or filled,

25 which maintain dimensional stability and most mechanical properties above 100°C and below 0°C. The terms "engineering plastics" and "engineering thermoplastics", can be used interchangeably. Engineering Thermoplastics include acetal resins, polyamides (e.g. nylons), polyimides, polyetherimides, polyesters, liquid crystal

30 polymers, and selected polyolefins, blends, or alloys of the foregoing resins, and some examples from other resin types (including e.g. polyethers) high temperature polyolefins such as polycyclopentanes, its copolymers, and polymethylpentane.)
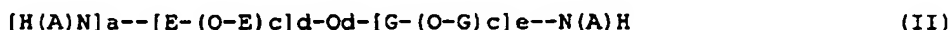
35   Concerning the Use of Amine-Functionalized Polymers as Subcomponent (c). One particularly suitable class of reactive thermoplastic polymers for use as subcomponent (c) is the class

33

923,255, filed October 27, 1986. In another suitable process, the
corresponding hydroxyl- or primary amine-terminated polyether or
polyester can be reacted in a transesterification reaction with a
material such as a lower alkyl ester of p-aminobenzoic acid,
5   particularly the methyl ester, to generate an aromatic polyamine
compound. Secondary aromatic polyamines can be prepared in a Michael
reaction of the corresponding primary aromatic amine compound and an
ethylenically unsaturated compound such as acrylonitrile, as described
above.

10   Blocked primary aliphatic polyamines suitable for use herein are
advantageously prepared in the reductive amination of the
corresponding hydroxyl-terminated compound with ammonia, followed by
the complexation thereof with a Lewis acid such as benzoyl chloride,
carbon dioxide, a metal carboxylate such as a tin, zinc, titanium or
15   aluminum carboxylate, and the like. The Lewis acid is advantageously
used in amounts of about 0.2 to about 5, and preferably about 0.9 to
about 1.5, equivalents per equivalent of primary amine group.

Various amine-functionalized polymers suitable for use herein
may be described by formula as:
20

        [H(A)N]a--Ea--(E-G-E)b--N(A)H   (I)

        [H(A)N]a--[E-(O-E)c]d-Od-[G-(O-G)c]e--N(A)H   (II)

25   [H(A)N]a--Q-[O-C(O)-Q-C(O)-O-Q]f--O-C(O)-Q-C(O)-O-Q--N(A)H (III)
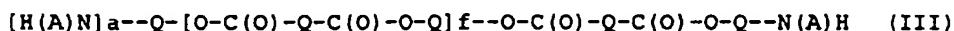
where
A   is independently in each instance hydrogen or a C_1-C_6 linear or
       branched alkyl or alkylene radical, optionally interruptable
30   with one or more nitrogen or oxygen atoms, wherein each carbon
       atom is optionally substituted with a primary or secondary amine
       group;
E   is independently in each instance a C_1-C_{20}, preferably a C_1-C_{12},
       and more preferably a C_1-C_8 linear, branched or cyclic alkyl or
35   alkylene radical, optionally interruptable with one or more
       nitrogen or oxygen atoms, wherein each carbon atom is optionally
       substituted with a halogen atom (such as a fluorine, chlorine,
       bromine or iodine atom), a C_1-C_6 alkoxy group, a C_6-C_{10} aryloxy

36

less than 250°C, and occasionally less than 230°C, or amorphous nylon.

Polyamides as described above, and methods for preparing same,
are discussed in greater detail in U.S. Pats. No. 2,071,253, 2,130,523
5   and 2,130,948.

Other varieties of amine-functionalized polymers include amine-
terminated butadiene/acrylonitrile rubber; or those polymers which
have one or more primary aromatic, Lewis acid-blocked primary
10 aliphatic and/or secondary aliphatic, or aromatic amine groups.
Especially suitable amine-functionalized polymers are polyethers or
polyesters having such amine groups.

Suitable polyols, especially polyether and polyester polyols,
15 which have secondary amine groups are conveniently prepared by
reacting the corresponding polyol with a primary amine, and reducing
the resulting intermediate with hydrogen, as described in U.S. Patent
No. 4,153,381. The secondary amine is advantageously an inertly
substituted alkyl-, cycloalkyl- or benzyl-amine. Alternatively,
20 secondary aliphatic polyamine compounds can be prepared in a Michael
addition reaction of the corresponding primary aliphatic amine with an
ethylenically unsaturated compound. Acrylonitrile is an especially
suitable ethylenically unsaturated compound, although any compound
which undergoes a Michael addition reaction with the primary amine can
25 be used. The primary aliphatic amine itself can be prepared in the
reductive amination of the corresponding polyol with ammonia, as
taught, for example, in U.S. Patent Nos. 3,128,311, 3,152,998,
3,654,370, 3,347,926, 4,014,933.

Other suitable amine-functionalized polymers are aromatic
30 polyamines, and include polyols, especially polyether and polyester
polyols, which have been modified to contain aromatic amine groups.
Such aromatic polyamines can be prepared, for example, by capping the
corresponding polyether or polyester polyol with a diisocyanate to
form a prepolymer, and then reacting the prepolymer with water to
35 hydrolyze the free isocyanate groups to the corresponding primary
amine. Alternatively, such compounds can be prepared by reacting the
corresponding polyether or polyester polyol with p-nitro
chlorobenzene, followed by the reduction of the nitro group to the
amine, as taught in the application of Steuber et al, Serial No.

35

                        30, inclusive;
    d and e   are both 0 or 1, although d and e cannot both be 0; and
    f   is 0 to 70, preferably 5 to 50, and more preferably 5 to
                        30, inclusive; or

5

    [H(A)N]a-(E-NH)j-(R2-G-R2-R3)h-R2-G-R2-(E-NH)j-N(A)H   (IV)
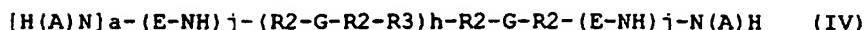
    where

10 R2   is independently in each instance an
                        -E-CH(OH)-E- radical;
    R3   is independently in each instance an
                        -HN-(E-NH)j- radical;
    A, E, G, a   are as set forth above;
15 h   is 0 to 25, preferably 0 to 10, and more preferably
                        1 to 3, inclusive; and
    j   is 1 to 6, and preferably 1 to 4, inclusive.

        Numerical variables in the above formulae may take on individual
20 values within the ranges specified or subranges other than those
    specifically set forth.

        The amine-functionalized polymer will have an average number of
    amine groups per molecule which is generally about 0.75 or more, is
25 preferably about 0.8 or more, is more preferably about 0.9 or more,
    and is most preferably about 1.0 or more. The amine-functionalized
    polymer will have an average number of amine groups per molecule which
    is generally about 3.5 or less, is preferably about 3.0 or less, is
    more preferably about 2.5 or less, and is most preferably about 2.1 or
30 less.

        The amine-functionalized polymer will typically have an
    equivalent weight (defined as weight average molecular weight divided
    by average number of amine groups) of about 400 to about 50,000,
35 preferably about 600 to about 30,000, and more preferably about 800 to
    about 20,000.

        The amine-functionalized polymer will be present in an
    amount sufficient to form the final block of. the branched block

group, a phenyl group, or a primary or secondary amine group;

G   is independently in each instance described by the following structure:

5
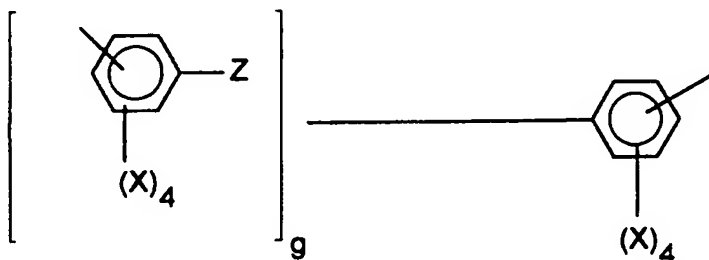
wherein:

   (1)   Z is (A) a divalent radical, of which all or different

10   portions can be (i) linear, branched, cyclic or bicyclic, (ii) aliphatic or aromatic, and/or (iii) saturated or unsaturated, said divalent radical being composed of 1-35 carbon atoms together with up to five oxygen, nitrogen, sulfur, phosphorous and/or halogen

15   (such as fluorine, chlorine and/or bromine) atoms, wherein each carbon atom is optionally substituted with a primary or secondary amine group; or (B) S, S_2, SO, SO_2, O or CO; or (C) a single bond, and

20   (II)   each X is independently hydrogen, a halogen atom (such as flourine, chlorine and/or bromine), a C_1-C_{12} linear or cyclic alkyl, alkoxy, aryl or aryloxy radical, such as methyl, ethyl, isopropyl, cyclopentyl, cyclohexyl, methoxy, ethoxy, benzyl, tolyl, xylyl, phenoxy and/or

25   xylynoxy; or primary or secondary amine group; and

   (III)   g is 0 or 1;

Q   is independently in each instance E or G;

30 a   is 0 or 1;

   b   is 0 to 10, preferably 0-4, and more preferably 1 to 3, inclusive, although a and b cannot both be 0;

   c   is 1 to 70, preferably 5 to 50, and more preferably 5 to

hydroxycarboxylic acids, or by direct esterification, which
involves the step-growth reaction of a diol with a dicarboxylic
acid with the resulting elimination of water, giving a polyester
with an -[-AABB-]- repeating unit. The reaction may be run in
5   bulk or in solution using an inert high boiling solvent such as
xylene or chlorobenzene with azeotropic removal of water.

Alternatively, but in like manner, ester-forming derivatives of
a dicarboxylic acid can be heated with a diol to obtain polyesters in
10   an ester interchange reaction. Suitable acid derivatives for such
purpose are alkyl esters, halides, salts or anhydrides of the acid.
Preparation of polyarylates, from a bisphenol and an aromatic diacid,
can be conducted in an interfacial system which is essentially the
same as that used for the preparation of polycarbonate.

15   Polyesters can also be produced by a ring-opening reaction of
cyclic esters or C_4-C_7 lactones, for which organic tertiary amine bases
phosphines and alkali and alkaline earth metals, hydrides and
alkoxides can be used as initiators.

Suitable reactants for making the polyester used in this
20   invention, in addition to hydroxycarboxylic acids, are diols and
dicarboxylic acids either or both of which can be aliphatic or
aromatic. A polyester which is a poly(alkylene alkanedicarboxylate),
a poly(alkylene arylenedicarboxylate), a poly(arylene
alkanedicarboxylate), or a poly(arylene arylenedicarboxylate) is
25   therefore appropriate for use herein. Alkyl portions of the polymer
chain can be substituted with, for example, halogens, C_1-C_8 alkoxy
groups or C_1-C_8 alkyl side chains and can contain divalent heteroatomic
groups (such as -O-, -Si-, -S- or -SO_2-) in the paraffinic segment of
the chain. The chain can also contain unsaturation and C_6-C_{10} non-
30   aromatic rings. Aromatic rings can contain substituents such as
halogens, C_1-C_8 alkoxy or C_1-C_8 alkyl groups, and can be joined to the
polymer backbone in any ring position and directly to the alcohol or
acid functionality or to intervening atoms.

40

ethylene polymers of the invention, without being present in such
a high quantity that the desired benefit of the branched block
ethylene polymer as a compositional modifier is sacrificed.
Typically, the amine-functionalized polymer is used in an amount
5   such that, after addition to the branched ethylene polymer to
form a branched ethylene block polymer, the portion of the
branched ethylene block polymer derived from the amine-
functionalized polymer constitutes by weight, at least about 1
percent, preferably at least about 2 percent, and more preferably
10   at least about 5 percent, and yet not more than about 40 percent,
preferably not more than about 30 percent, and more preferably
not more than about 25 percent of the branched block ethylene
polymer.

15   For example, it would not ordinarily be expected that a
crystalline, polar, amine-functionalized polymer such as
polyamide would improve the performance of a non-polar ethylene
polymer as a modifier in a blend with a thermoplastic molding
polymer. However, it has been found that when an amine-
20   functionalized polymer, such as polyamide, is used in the amounts
stated above, it not only forms the final block of the branched
block ethylene polymer, but remains morphologically dispersed
within domains formed by an ethylene/vinyl compound copolymer.
However, if an amine-functionalized polymer such as polyamide is
25   used in amounts exceeding the above-recommended amounts, it tends
to form crystalline domains of its own in which an ethylene/vinyl
compound copolymer is dispersed, and the brittleness of those
polyamide domains offsets the gain in impact strength which a
block terpolymer would otherwise impart to the blended
30   composition. Correspondingly, if an amine-functionalized polymer
which has too high an average amine functionality is used,
crosslinking is likely to occur.

     Concerning the Use of a Polyester as the Reactive
35   Thermoplastic Polymer of Component (c):

     A further class of reactive thermoplastic polymers useful
as subcomponent (c) of the branched block ethylene polymers are
polyesters. Polyesters may be made by the self-esterification of

Methods and materials useful for the production of polyesters,
as described above, are discussed in greater detail in Whinfield, USP
2,465,319, Pengilly, USP 3,047,539, Schwarz, USP 3,374,402, Russell,
USP 3,756,986 and East, USP 4,393,191.

5

In a preferred embodiment, a polyester is used in an amount
such that, after addition to an ethylene/vinyl compound copolymer
to form a branched block ethylene polymer, the portion of the
branched block ethylene polymer derived from the polyester

10   constitutes by weight, at least about 1 percent, preferably at
least about 2 percent, and more preferably at least about 5
percent, and yet not more than about 30 percent, preferably not
more than about 20 percent, and more preferably not more than
about 10 percent of the branched block ethylene polymer. In

15   other embodiments, when for example a catalyst is used to
accelerate formation of a branched block ethylene polymer, the
amount of polyester used may constitute more than about 60,
possibly more than about 70, or perhaps more than about 80 weight
percent of the branched block ethylene polymer, but values

20   outside these ranges are permitted as well. In a further
preferred embodiment, the polyester is used in an amount such
that the weight ratio between the amount of polyester contained
in the branched block ethylene polymer and the amount of blending
or molding polymer contained in the composition is greater than

25   about 0.01/1, is often greater than about 0.015/1, and
occasionally greater than about 0.02/1, and yet is less than
about 0.30/1, is often less than about 0.15/1, and is
occasionally less than 0.10/1.

30   In a further preferred embodiment, the polyester used for
preparation of a branched block ethylene polymer has an intrinsic
viscosity (IV) of less than about 0.85, advantageously about 0.5
to about 0.8, and preferably about 0.55 to about 0.75. A
polyester having a relatively low IV is in general composed of

35   shorter polymer chains than a polyester of relatively high IV. A
particular mass of low IV polyester will therefore contain more

42

Typical aliphatic diols used in ester formation are the C_2-C_{10} primary and secondary glycols, such as ethylene-, propylene-, and butylene glycol. Alkanedicarboxylic acids frequently used are oxalic acid, adipic acid and sebacic acid. Diols which contain rings can be,

5   for example, a 1,4-cyclohexylenyl glycol or a 1,4-cyclohexane-dimethylene glycol, resorcinol, hydroquinone, 4,4'-thiodiphenol, bis-(4-hydroxyphenyl)sulfone, a dihydroxynaphthalene, a xylylene diol, or can be one of the many bisphenols such as 2,2-bis-(4-hydroxyphenyl)propane. Aromatic diacids include, for example,

10   terephthalic acid, isophthalic acid, naphthalenedicarboxylic acid, diphenyletherdicarboxylic acid, diphenyldicarboxylic acid, diphenylsulfonedicarboxylic acid, diphenoxyethanedicarboxylic acid.

In addition to polyesters formed from one diol and one diacid only, the term "polyester" as used herein includes random, patterned

15   or block copolyesters, for example those formed from two or more different diols and/or two or more different diacids, and/or from other divalent heteroatomic groups. Mixtures of such copolyesters, mixtures of polyesters derived from one diol and diacid only, and mixtures of members from both of such groups, are also all suitable

20   for use in this invention, and are all included in the term "polyester". For example, use of cyclohexanedimethanol together with ethylene glycol in esterification with terephthalic acid forms a clear, amorphous copolyester of particular interest. Also contemplated are liquid crystalline polyesters derived from mixtures

25   of 4-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid; or mixtures of terephthalic acid, 4-hydroxybenzoic acid and ethylene glycol; or mixtures of terephthalic acid, 4-hydroxybenzoic acid and 4,4'-dihydroxybiphenyl.

Aromatic polyesters, those prepared from an aromatic diacid,

30   such as the poly(alkylene arylenedicarboxylates) polyethylene terephthalate and polybutylene terephthalate, or mixtures thereof, are particularly useful in this invention. A polyester suitable for use herein may have an intrinsic viscosity of about 0.4 to 1.2, although values outside this range are permitted as well.

41

When using an extruder for preparation of a branched block
ethylene polymer, the separate components from which it is prepared
are typically fed in sequence through separate ports during a single
pass through one extruder for more convenient material handling. If
5   the ethylene polymer, ethylenically unsaturated organic compound, and
reactive thermoplastic polymer are reacted simultaneously, it is
probable that the ethylenically unsaturated organic compound will form
an insignificant amount of branching on the ethylene polymer, or none
at all, because the presence of the reactive thermoplastic polymer can
10   physically hinder the necessary access of unsaturated organic compound
for branch formation.

The Use of Catalysts in the Preparation of the Block Ethylene Polymers
of the Invention:

15

Reaction between the branched ethylene polymer and the reactive
thermoplastic polymer to complete preparation of the branched block
ethylene polymers of the invention is optionally enhanced by the
presence of a catalyst. Such catalysts may include an alkali metal or
20   alkaline earth metal salt having a pKa of 7 or more and a nitrogen-
containing organic base. Those catalysts which melt at or below the
temperature at which the branched ethylene polymer and reactive
thermoplastic polymer are being reacted, and which have low volatility
at that temperature, will be most effective.

25

Salts having a pKa of 7 or more, useful as a catalyst herein,
are those formed from cations of which the following are
representative examples:
lithium, sodium, potassium, magnesium, calcium or barium;
30   and from anions of which the following are representative examples:
azide, acetate, benzoate, borate, bromate, bromide, carbonate,
carboxylate, chlorate, chloride, chlorite, chromate, cyanate,
cyanide, dithionate, fluoride, formate, hydrogen carbonate,
hydrogen phosphate, hydrogen sulfate, hydrogen sulfide, hydrogen
35   sulfite, hydroxide, hypophosphate, hypophosphite, iodate,
iodide, iodite, molybdate, nitrate, nitrite, oxalate, oxide,

44

chain end groups than will the same mass of high IV polyester.
Since formation of a branched block ethylene polymer is dependent
on the reaction of polyester end groups, especially -OH end
groups, with the branch point formed from a vinyl compound on an
5   ethylene polymer, it is advantageous to use a polyester for this
purpose which contains a relatively large number of end groups.

Process for Preparing the Branched Block Ethylene Polymers of the Invention:

10

The branched block ethylene polymers of this invention are
prepared by first forming a branch containing the ethylenically
unsaturated functionalized organic compound off of the ethylene
polymer. This may be accomplished by the techniques set forth above,
15   e.g., using the methods of graft polymerization taught in USP
3,236,917, USP 5,194,509, and/or USP 4,950,541.

After the ethylenically unsaturated functionalized organic
compound, such as maleic anhydride, has been formed into a branch off
20   of the ethylene polymer, preparation of the branched block ethylene
polymer of this invention can be completed by subjecting the branched
ethylene polymer and the reactive thermoplastic polymer to reactive
extrusion. Reactive end groups on the reactive thermoplastic polymer
react in the melt state with the functionality of the functionalized
25   organic compound branch to form a chemical bond and add the final
polymer block to the branched block ethylene polymers of this
invention. This reaction between reactive thermoplastic polymer and
the branch formed from the ethylenically unsaturated functionalized
organic compound may be enhanced by a catalyst, if desired. Although
30   this reaction optionally occurs in a Banbury mixer or other apparatus
in which elevated temperature and high shear mixing can be applied to
the reactants, a representative profile for conducting this reaction
in a 30 mm twin screw extruder is: zone temperatures of 150, 200, 250,
250 and 250°C; 250 rpm; 70-85 percent torque; and 30 second
35   residence time.

based on the combined weight of the branched ethylene polymer and the
reactive thermoplastic polymer.

Concerning the Blending of the Branched Block Ethylene Polymers with
5   an Additional Blending or Molding Polymer:

The branched block ethylene polymers of the invention may
advantageously be dry blended or melt blended with one or more
additional blending or molding polymers. In one instance the branched
10   block ethylene polymer will be dry blended or melt blended with a
blending or molding, and then molded or extruded into a shaped
article.

It is noted from the exemplary polymers shown in the Figures
.15 that branched block ethylene polymers of the invention are effective
rheology modifiers, effective melt strength enhancers, blow molding or
thermoforming strength enhancers, effective oil extended polymers,
and/or impact modifiers.

20   It is further noted that the formation of a random,
physical blend from a ethylene polymer which has been graft-
modifed by an ethylenically unsaturated functionalized monomer, a
reactive thermoplastic polymer and a thermoplastic blending or
molding polymer, is separate and distinct from the blend of a
25   branched block ethylene polymer and such blending or molding
polymer. The distinction can be appreciated by examining systems
comprising an ethylene polymer, ethylenically unsaturated
functionalized monomer, amine-functionalized polymer, and
blending or molding thermoplastic polymer.
30

In the case of a random, physical blend, an ethylene
polymer which has been graft modified with the ethylenically
unsaturated functionalized polymer may be used as an essentially
elastomeric modifier for one or more thermoplastic polymers, one
35   of which might be an amine-functionalized polymer. In the case
where two or more thermoplastic polymers are present in the
composition, the ethylene polymer which has been graft modified
with the ethylenically unsaturated functionalized polymer will

46

perchlorate, permanganate, phosphate, phosphite, pyrophosphate,
selenate, silicate, sulfate, sulfimide, sulfite, sulfonate,
thiocarbonate, thiocyanate, thiosulfate, and the like, in both
substituted and unsubstituted form, and derivatives thereof.

5

A preferred salt for use as a catalyst herein may be derived
from an aromatic sulfimide, as shown in the following structure where
M^+ is an alkali metal ion, for example potassium ion.

$$Ar-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-N^-\quad M^+$$
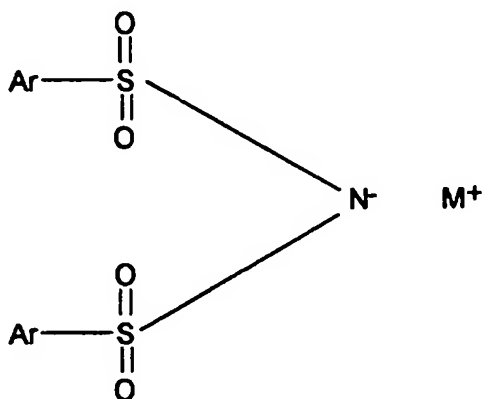
10

Representative nitrogen-containing organic bases useful as a
catalyst herein may include acridine, analine, aziridine, benzidine,
15   benzimidazole, isoquinoline, morpholine, picoline, piperazine,
piperidine, purine, pyrazine, pyridine, pyrimidine, pyrrolidine,
quinazoline, quinoline, toluidine, valine, and the like. In general,
many aliphatic and aromatic amines, in both substituted and
unsubstituted form, and derivatives thereof, may serve as a catalyst
20   herein, the most common being tertiary amines such as triethylamine
and pyridine.

The amount of the catalyst used in preparation of the branched
block ethylene polymers of the invention is, by weight, at least about
25   100 ppm, and preferably at least about 1,000 ppm, and yet not more
than about 3,000 ppm, and preferably not more than about 2,000 ppm,

45

copolymer, polyisobutylene, ethylene-propylene-diene monomer (EPDM), polystyrene, acrylonitrile-butadiene-styrene (ABS) copolymer, ethylene/acrylic acid (EAA), ethylene/vinyl acetate (EVA), ethylene/vinyl alcohol (EVOH), polymers of ethylene and carbon

5 monoxide (ECO, including those described in USP 4,916,208), or ethylene, propylene and carbon monoxide (EPCO) polymers, or ethylene, carbon monoxide and acrylic acid (ECOAA) polymers, and the like. Representative of the non-olefin blending or molding polymers are the polyesters, polyvinyl chloride (PVC), epoxies, polyurethanes,

10 polycarbonates, polyamides, and the like.

The exemplary blending or molding polymers are characterized by a compatibility with the branched block ethylene polymer such that the melt blend does not separate into separate polymer phases. If more

.15 than one of these blending or molding polymers is blended with one or more branched block ethylene polymers, then all usually exhibit sufficient compatibility with each other, one-to-one or at least in combination with one or more other polymers, such that the polymeric components do not separate into separate polymer phases which could

20 lead to extrusion processing difficulties, such as extrudate surging, film band-effects, etc.

The amount of branched block ethylene polymer that is blended with one or more other blending or molding thermoplastic polymers can

25 be varied and is dependent upon many factors, including the nature of the blending or molding thermoplastic polymer or polymers, the intended end use of the blend, the presence or absence and if present, the nature, of additives, and the like.

30   Typically, the blend will comprise at least 1 part, advantageously at least about 2 parts, and preferably at least about 5 parts, and yet not more than about about 50 parts, advantageously not more than about 40 parts, and preferably not more than about 30 parts of the branched block ethylene polymer. Likewise, the blend will

35 typically comprise at least about 50 parts, advantageously at least about 60 parts, and preferably at least about 70 parts, and yet not

48

typically serve as such elastomeric modifier for each
thermoplastic polymer to an essentially equal extent.   In
contrast, when it is desired to use a branched block ethylene
polymer as a modifier in a blend with a thermoplastic blending or
5   molding polymer, if a branched block ethylene polymer is not
successfully formed, the result is no different from a random,
physical blend containing some amine-functionalized polymer as
one of the molding polymers in which the ethylene polymer which
has been graft-modified with the ethylenically unsaturated
10   functionalized polymer serves as modifier for the entire content
of molding polymer.

     The reactive thermoplastic polymer is present first and foremost
to alter the viscoelastic properties of the ethylene polymer which has
15   been graft-modified with the ethylenically unsaturated functionalized
monomer, and convert what was an essentially elastomeric modifier into
a hard segment/soft segment modifier. The reactive thermoplastic
polymer constitutes the hard segment, and the ethylene polymer
constitutes the soft segment. This hard segment/soft segment
20   modifier, thebranched block ethylene polymer, then serves as a modifer
for one or more blending or molding polymers. The reactive
thermoplastic polymer in thein the branched block ethylene polymer, as
an integral portion of the hard segment/soft segment modifier,
performs a function which is distinct from that of being just another
25   molding polymer in a random, physical blend.

     Suitable blending or molding polymers include any polymer with
which the branched block ethylene polymer is compatible, and include
both olefin and non-olefin polymers, grafted and ungrafted. The
branched block ethylene polymer can also be blended with a
30   substantially linear ethylene polymer, a conventional heterogeneously
branched or homogeneously branched linear ethylene polymer, a non-
olefin polymer, any of which can be grafted or ungrafted, or any
combination of these polymers.

35   Exemplary blending or molding polymers include high density
polyethylene (HDPE), low density polyethylene (LDPE), linear low
density polyethylene (LLDPE), ultra low density polyethylene (ULDPE),
polypropylene, ethylene-propylene copolymer, ethylene-styrene

47

1.5 MPa (5-15 atm), and the gas-phase and liquid-monomer processes, in which extra care must be given to the removal of amorpohous polymer. Ethylene may be added to the reaction to form a polypropylene with ethylene blocks.

5

Various higher olefins can be homopolymerized to form polyolefin resins using Ziegler-Natta catalysts, representative examples thereof being 1-butene, 1-methyl-pentene and 4-methyl-1-pentene. The polyolefin resins useful herein also include various ethylene

10 copolymers such as ethylene/acrylic acid copolymer, ethylene/vinyl acetate copolymer, ethylene/vinyl alcohol copolymer, ethylene/carbon monoxide copolymer (including those described in USP 4,916,208 and 4,929,673, ethylene/propylene/carbon monoxide copolymer, ethylene/carbon monoxide/acrylic acid copolymer, poly(vinyl chloride),

15 and the like and mixtures thereof. For example, in the suspension process for preparing poly(vinyl chloride), vinyl chloride monomer can be copolymerized with other vinyl monomers, such as vinyl acetate, acrylonitrile, butadiene, butyl acrylate, maleic anhydride, an olefin or styrene, to produce a random, block or graft copolymer.

20

One particular advantage of using a polyamide resin, as the molding polymer is that it can be blended with a block terpolymer in a molding machine, and the addition of an extra heat history to the composition by first extruding pellets of a block terpolymer/molding

25 polymer composition is thus avoided.

Use of Polyamides as the Blending or Molding Polymer. Polyamides useful as the thermoplastic polymer are described above as a variety of amine-functionalized polymer which may be used in preparation of a

30 block terpolymer. When a polyamide is used as the molding polymer, it is possible, and sometimes preferred, to use a different polyamide from that which was used to prepare the block terpolymer. For example, the polyamide used to prepare the block terpolymer may be a Nylon 6, whereas the polyamide used as the molding polymer may be a

35 Nylon 6,6; 6,10; or 12, and/or the blending or molding polymer may have an average number of amine groups greater than about 2.0, or in the range of about 2.05 to about 3.5. One particular advantage of using a polyamide resin, as the molding polymer is that it can be blended with a block terpolymer in a molding machine, and the addition

50

more than about about 99 parts, advantageously not more than about 98
parts, and preferably not more than about 95 parts, of the blending or
molding thermplastic polymer or polymers. Note that the number of
parts by weight of the branched block ethylene polymer and the
5   blending or molding polymer or polymers may, but need not necessarily,
total 100 parts by weight.

However, if the blending or molding polymer is identical in
composition of the reactive thermoplastic polymer which forms a branch
10 of the branched block ethylene polymer, the total amount of the
reactive thermoplastic polymer and blending or molding thermpolastic
polymer will exceed 30 parts, preferably 20 parts, more preferably 15
parts, and most preferably 10 parts, per 100 weight parts of the
blended composition.

15

Preferred blending or molding polymers for use in conjunction
with a branched block ethylene polymer which has as the reactive
thermoplastic polymer a functionalized-amine polymer include (i)
polyolefin resins, (ii) a polyamide, (iii) a polycarbonate, (iv) a
20 hydrogenated polystyrene; and (v) a mixture thereof. Preferred
blending or molding polymers for use in conjunction with a branched
block ethylene polymer which has as the reactive thermoplastic polymer
a polyester include (i) a polycarbonate, (ii) a polyester, (iii) a
poly(phenylene ether), (iv) a polysulfone, (v) a polyimide or
25 polyether imide, and (vi) a mixture thereof.

Use of Polyolefin Resins as the Blending or Molding Polymer.
Polyolefin resins useful as the thermoplastic polymer are any of the
ethylene polymers described above with respect to preparation of
30 branched block ethylene polymer, and polypropylene. The preparation
of polypropylene also involves the use of Ziegler catalysts, which
allows the stereo regular polymerization of propylene to form
isotactic polypropylene. The catalyst used is typically a titanium
trichloride in combination with aluminum diethylmonochloride, as
35 further described in Cecchin, USP 4,177,160. The various types of
polymerization processes used for the production of polypropylene
include the slurry process, which is run at about 50 - 90°C and 0.5 -

49

phosgene, the products of this initial phase of the process are monomers or oligomers which are either mono- or dichloroformates, or contain a phenolate ion at each terminus.

5   These intermediate mono- and oligocarbonates dissolve in the organic solvent as they form, and they can then be condensed to a higher molecular weight polycarbonate by contact with a coupling catalyst of which the following are representative: a tertiary amine such as triethyl amine and dimethyl amino pyridine.

10

        Upon completion of polymerization, the organic and aqueous phases are separated to allow purification of the organic phase and recovery of the polycarbonate product therefrom. The organic phase is washed as needed in a centrifuge with dilute base, water and/or dilute acid

15   until free of unreacted monomer, residual process chemicals and/or other electrolytes. Recovery of the polycarbonate product can be effected by spray drying, steam devolatilization, direct devolatilization in a vented extruder, or precipitation by use of an anti-solvent such as toluene, cyclohexane, heptane, methanol, hexanol,

20   or methyl ethyl ketone.

        In the melt process for preparation of polycarbonate, aromatic diesters of carbonic acid are condensed with an aromatic dihydroxy compound in a transesterification reaction in the presence of a basic

25   catalyst. The reaction is typically run at about 250°C to 300°C under vacuum at a progressively reduced pressure of about 1 to 100 mm Hg.

        Polycarbonate can also be prepared in a homogeneous solution through a process in which a carbonate precursor, such as phosgene, is

30   contacted with a solution containing an aromatic dihydroxy compound, a chlorinated hydrocarbon solvent and a substance, such as pyridine, for dimethyl aniline or Ca(OH)$_2$, which acts as both acid acceptor and condensation catalyst.

35   Examples of some dihydroxy compounds suitable for the preparation of polycarbonate include variously bridged, substituted or unsubstituted aromatic dihydroxy compounds (or mixtures thereof)

of an extra heat history to the composition by first extruding pellets
of a block terpolymer/molding polymer composition is thus avoided.

Use of Polycarbonates as the Blending or Molding Polymer.

5   Polycarbonates useful as the blending or molding polymer can be
prepared from a dihydroxy compound such as a bisphenol, and a
carbonate precursor such as a disubstituted carbonic acid derivative,
a haloformate (such as a bishaloformate of a glycol or dihydroxy
benzene), or a carbonate ester such as diphenyl carbonate or a
10   substituted derivative thereof. These components are often reacted by
means of the phase boundary process in which the dihydroxy compound is
dissolved and deprotonated in an aqueous alkaline solution to form
bisphenolate and the carbonate precursor is dissolved in an organic
solvent.

15

These components are often reacted by means of a mixture prepared
initially from the aromatic dihydroxy compound, water and a non-
reactive organic solvent immiscible with water selected from among
those in which the carbonate precursor and polycarbonate product are
20   soluble. Representative solvents include chlorinated hydrocarbons
such as methylene chloride, 1,2-dichloroethane, tetrachloroethane,
chlorobenzene, and chloroform. Caustic soda or other base is then
added to the reaction mixture to adjust the pH of the mixture to a
level at which the dihydroxy compound is activated to dianionic form.

25

A carbonate precursor is contacted with an agitated mixture of
the aqueous alkaline solution of the dihydroxy compound, and, for such
purpose, the carbonate precursor can be bubbled into the reaction
mixture in the form of a gas, or can be dissolved and introduced in
30   solution form. Carbonater precursor is typically used in an amount of
about 1.0 to 1.8, preferably about 1.2. to 1.5, moles per mole of
dihydroxy compound. The mixture is agitated in a manner which is
sufficient to disperse or suspend droplets of the solvent containing
the carbonate precursor in the aqueous alkaline solution. Reaction
35   between the organic and aqueous phases created by such agitation
yields the bis(carbonate precursor) ester of the dihydroxy compound.
For example, if the carbonate precursor is a carbonyl halide such as

hydroxyphenyl)propane ("Bisphenol-A" or "Bis-A");   2,2-bis(3,5-dihalo-
4-hydroxyphenyl)propane ("Tetrahalo Bisphenol-A") where the halogen
can be fluorine, chlorine, bromine or iodine, for example 2,2-bis(3,5-
dibromo-4-hydroxyphenyl)propane ("Tetrabromo Bisphenol-A" or "TBBA");

5   2,2-bis(3,5-dialkyl-4-hydroxyphenyl)propane ("Tetraalkyl Bisphenol-A")
where the alkyl can be methyl or ethyl, for example 2,2-bis(3,5-
dimethyl-4-hydroxyphenyl)propane ("Tetramethyl Bisphenol-A");   1,1-
bis(4-hydroxyphenyl)-1-phenyl ethane ("Bisphenol-AP" or "Bis-AP");
Bishydroxy phenyl fluorene; and 1,1-bis(4-hydroxyphenyl)cyclohexane.

10

        Using a process such as is generally described above, a
polycarbonate product can be obtained having a weight average
molecular weight, as determined by light scattering or gel permeation
chromatography, of 8,000 to 200,000 and preferably 15,000 to 40,000,

15   and/or a melt flow value of about 3 to 150, preferably about 10 to 80
(as determined by ASTM Designation D 1238-89, Condition 300/1.2),
although values outside these ranges are permitted as well. Molecular
weight can be controlled by addition to the reaction mixture of a
chain terminator which may be selected from monofunctional substances

20   such as phenols, carbonic acid chlorides, or phenylchlorocarbonates.

        A branched rather than linear polycarbonate molecule can be
obtained by adding to the reaction mixture a tri- or polyfunctional
monomer such as trisphenoxy ethane.

25

        The preferred process of this invention is that in which an
aromatic polycarbonate is prepared. An aromatic polycarbonate is
defined herein with reference to the oxygen atoms, of the one or more
dihydroxy compounds present in the polycarbonate chain, which are

30   bonded to a carbonyl carbon of the carbonate precursor. In an
aromatic polycarbonate, all such oxygen atoms are bridged by a
dihydroxy compound residue some portion of which is an aromatic ring.

        Also included within the term "polycarbonate", as used herein,

35   are various copolycarbonates, certain of which can be prepared by
incorporating one or more different dihydroxy compounds into the
reaction mixture. When a dicarboxylic acid such terephthalic acid or

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represented by the formula:

H—⟨○⟩—[—Z—⟨○⟩—O]ₘ

(X)₄   (X)₄
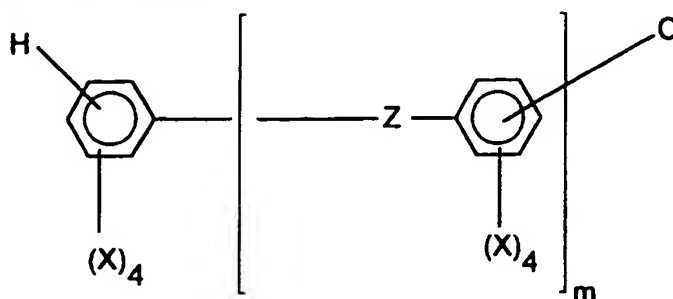
wherein:

I)   Z is (A) a divalent radical, of which all or different
    5   portions can be (i) linear, branched, cyclic or bicyclic, (ii)
        aliphatic or aromatic, and/or (iii) saturated or unsaturated,
        said divalent radical being composed of 1-35 carbon atoms
        together with up to five oxygen, nitrogen, sulfur, phosphorous
        and/or halogen (such as fluorine, chlorine and/or bromine)
   10   atoms; or (B) S, S_2, SO, SO_2, O or CO; or (C) a single bond;

II)   each X is independently hydrogen, a halogen (such as fluorine,
        chlorine and/or bromine), a C_1-C_{12}, preferably C_1-C_8, linear or
        cyclic alkyl, aryl, alkaryl, aralkyl, alkoxy or aryloxy
   15   radical, such as methyl, ethyl, isopropyl, cyclopentyl,
        cyclohexyl, methoxy, ethoxy, benzyl, tolyl, xylyl, phenoxy
        and/or xylynoxy; or a nitro or nitrile radical; and

(III) m is 0 or 1.
20

      For example, the bridging radical represented by Z in the above
formula can be a C_2-C_{30} alkyl, cycloalkyl, alkylidene or cycloalkyidene
radical, or two or more thereof connected by an aromatic or ether
linkage, or can be a carbon atom to which is bonded one or more groups
25   such as CH_3, C_2H_5, C_3H_7, n-C_3H_7, i-C_3H_7, cyclohexyl,
bicyclo[2.2.1]heptyl, benzyl, CF_2, CF_3 CCl_3, CF_2Cl, CN, $(CH_2)_2COOCH_3$, or
$PO(OCH_3)_2$.

      Representative examples of dihydroxy compounds of particular
30   interest are the bis(hydroxyphenyl)alkanes, the
bis(hydroxyphenyl)cycloalkanes, the dihydroxydiphenyls and the
bis(hydroxyphenyl)sulfones, and in particular are 2,2-bis(4-

Use of Poly(phenylene ether) as the Thermoplastic Polymer.

Suitable thermoplastic polymers include poly(phenylene ether)
[also known as a poly(phenylene oxide)], which is a polymer
comprising a plurality of structural units described generally by

5   the formula:
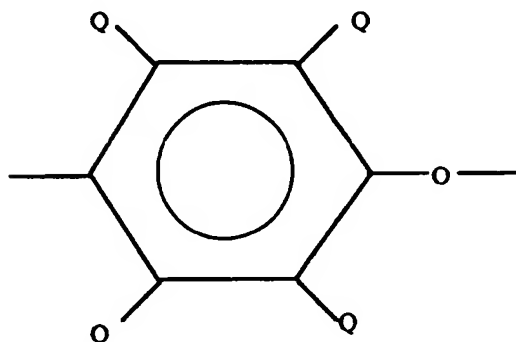
In each of said units independently, each Q_1 is independently

10   hydrogen, halogen, primary or secondary

C_1-C_8 lower alkyl, phenyl, haloalkyl, aminoalkyl, hydrocarbonoxy, or
halohydrocarbonoxy wherein at least two carbon atoms separate the
halogen and oxygen atoms; and each Q_2 is independently hydrogen,
halogen, primary or secondary C_1-C_8 lower alkyl, phenyl, haloalkyl,

15   hydrocarbonoxy or halohydrocarbonoxy as defined for Q_1. Examples of
suitable primary lower alkyl groups are methyl, ethyl, n-propyl, n-
butyl, isobutyl, n-amyl, isoamyl, 2-methylbutyl, n-hexyl, 2,3-
dimethylbutyl, 2-, 3- or 4-methylpentyl and the corresponding heptyl
groups. Examples of secondary lower alkyl groups are isopropyl, sec-

20   butyl and 3-pentyl. It is preferred that any alkyl radicals are
straight chain rather than branched. Most often, each Q_1 is alkyl or
phenyl, especially C_1-C_4 alkyl, and each Q_2 is hydrogen.

Both homopolymer and copolymer poly(phenylene ether)s are

25   included, as well as mixtures or blends thereof. Suitable

56

isophthalic acid (or an ester-forming derivative thereof) or a
hydroxycarboxylic acid is used in the reaction mixture, or to form an
oligomeric prepolymer, instead of one of the "different" dihydroxy
compounds mentioned above, a poly(ester/carbonate) is obtained, which
5   is discussed in greater detail in Swart, USP No. 4,105,533. In a
preferred embodiment, the compositions of this invention exclude a
poly(ester/carbonate).

Copolycarbonates can also be prepared, for example, by reaction
10   of one or more dihydroxy compounds with a carbonate precursor in the
presence of a chlorine- or amino-terminated polysiloxane, with a
hydroxy-terminated poly(phenylene oxide) or poly(methyl methacrylate),
or with phosphonyl dichloride or an aromatic ester of a phosphonic
acid. Siloxane/carbonate block terpolymers are discussed in greater
· 15 detail in Paul, USP 4,596,970.

The methods generally described above for preparing
carbonate polymers suitable for use in the practice of this
invention are well known; for example, several methods are
20   discussed in detail in Schnell, USP 3,028,365; Glass, USP
4,529,791; and Grigo, USP 4,677,162.

Use of a Polyester as the Blending or Molding Polymer.
When a polyester is used as a blending or molding polymer in the
25   blend compositions of this invention, the polyester will be as
described above as subcomponent (c) with respect to preparation
of the branched block ethylene polymer. It is preferred that a
polyester used as the blending or molding polymer in the blend
compositions of this invention have an intrinsic viscosity of
30   about 0.85 or more, advantageously about 0.9 to about 1.2, and
preferably about 0.95 to about 1.05.
It is further preferred that when a polyester is used both
as subcomponent (c) of the branched block ethylene polymer and as
the blending or molding polymer, a different polyester be used
35   for each.

trimethylphenol (wherein each Q_1 and one Q_2 is methyl and the other Q_2 is hydrogen). A variety of catalyst systems are known for the preparation of poly(phenylene ether)s by oxidative coupling. For the most part, they contain at least one heavy metal compound such as a

5   copper, manganese or cobalt compound, usually in combination with various other materials. A first class of preferred catalyst systems consists of those containing a copper compound, such as are disclosed, for example, in U.S. Pat. Nos. 3,306,874, 3,306,875, 3,914,266 and 4,028,341. They are usually combinations of cuprous or cupric ions,

10 halide (i.e., chloride, bromide or iodide) ions and at least one amine. Catalyst systems containing manganese compounds constitute a second preferred class. They are generally alkaline systems in which divalent manganese is combined with such anions as halide, alkoxide or phenoxide. Most often, the manganese is present as a complex with one

15 or more complexing and/or chelating agents such as dialkylamines, alkanolamines, alkylenediamines, o-hydroxyaromatic aldehydes, o-hydroxyazo compounds, w-hydroxyoximes (monomeric and polymeric), o-hydroxyaryl oximes and ß-diketones. Also useful are known cobalt-containing catalyst systems.

20

Poly(phenylene ether)s, as described above, are discussed in greater detail in U.S. Pat. No. 4,866,130.

Also included in the category of poly(phenylene ether)s is a

25 poly(phenylene ether) blend which is prepared by blending a poly(phenylene ether) with polystyrene, a vinyl aromatic copolymer, and/or with other non-styrenic polymers as specified below. When the thermoplastic polymer used as a blending or molding polymer is a poly(phenylene ether) blend, such blend will be made up of about 20 to

30 about 99 parts poly(phenylene ether), preferably about 30 to 90 parts poly(phenylene ether), by weight, with the balance being made up of polystyrene, a vinyl aromatic copolymer, and/or the non-styrenic polymers. A preferred such formulation contains about 30 to about 85 weight parts poly(phenylene ether), about 15 to about 70 weight parts

35 selected from one or more of the following: polystyrene, high impact

58

homopolymers are those containing, for example, 2,6-dimethyl-1,4-phenylene ether units. Suitable copolymers include random copolymers containing such units in combination with, for example, 2,3,6-trimethyl-1,4-phenylene ether units.

5

Also included are poly(phenylene ether) containing moieties which modify properties such as molecular weight, melt viscosity and/or impact strength. Such polymers may be prepared by copolymerizing with or grafting onto the poly(phenylene ether), in known manner, such

10 vinyl monomers as vinyl nitrile compounds (e.g. acrylonitrile) and vinyl aromatic compounds (e.g., styrene), or such polymers as polystyrenes and elastomers. The product typically contains both grafted and ungrafted moieties. Other suitable polymers are the coupled poly(phenylene ether)s in which the coupling agent is reacted,

15 in known manner, with the hydroxy groups of two poly(phenylene ether) chains to produce a higher molecular weight polymer containing the reaction product of the hydroxy groups and the coupling agent. Illustrative coupling agents are low molecular weight polycarbonates, quinones, heterocycles, formals and poly(phenylene sulfide)s. For

20 example, poly(phenylene ether)/polycarbonate copolymers are known and are discussed in U.S. Pat. No. 5,010,143.

The poly(phenylene ether) typically has a number average molecular weight within the range of about 3,000-40,000, and a weight

25 average molecular weight within the range of about 20,000-80,000, as determined by gel permeation chromatography. Its intrinsic viscosity is typically in the range of about 0.15-0.6, and preferably at least 0.25, dL/g, as measured in chloroform at 25°C. However, values outside these ranges are permitted as well.

30

The poly(phenylene ether)s are typically prepared by the oxidative coupling of at least one corresponding monohydroxyaromatic compound. Particularly useful and readily available monohydroxyaromatic compounds are 2,6-xylenol (wherein each Q_1 is

35 methyl and each Q_2 is hydrogen), whereupon the polymer may be characterized as a poly(2,6-dimethyl-1,4-phenylene ether), and 2,3,6-

57

Another variety of polysulfone is synthesized from a bisphenol
which itself contains a sulfone bride ("Bisphenol-S"). This
polymerization is run at a higher temperature (up to about 285°C), in
a dipolar aprotic solvent such as diphenyl sulfone and employs a base
5   such as sodium or potassium carbonate. Removal of water is typically
not a concern. This type of polymer is available from ICI Americas,
Inc. as Victrex™ polysulfone.

Other bisphenols which have been used to prepare polysulfone are
10   4,4'-dihydroxydiphenyl sulfide, 4,4'-dihydroxydiphenyl oxide, 4,4'-
dihydroxydiphenylmethane, hydroquinone, bis(4-hydroxydiphenyl)-2,2-
perfluoropropane, bis(4-hydroxydiphenyl)-1,1-cyclohexane, 4,4'-
dihydroxybenzophenone, and 4,4'-dihydroxydiphenyl.

15   In general, the repeating unit of a polysulfone may be
represented generally by structure as follows:

$$--[--Ar--S(O)_2--Ar--O--Ar(X)_4--[--Z--Ar(X)_4--]q--O--]p--$$
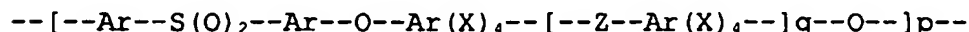
20   where Ar, D and E are as set forth above, q is about 0 to about 3 and
p is about 10 to about 100.

Use of Polyimide or Polyetherimide as the Blending or
Molding Polymer. A polyimide is a condensation polymer derived
25   from a bifunctional carboxylic acid anhydride and a primary
diamine. Two equivalents of water are liberated by formation of
the imide bond, one in the formation of the anhydride ring and
the second as a result of displacement of oxygen in the ring by
nitrogen. The polymer can alternatively be prepared by reaction
30   of a diamime directly with a tetracarboxylic acid. In either
event, an intermediate is obtained, for example polyamic acid
when the starting material is an anhydride, and the second
equivalent of water is liberated by heating to form polymer.
Reaction of a dianhydride and a diamine to form the polyamic acid
35   intermediate occurs at ambient temperatures in a dipolar aprotic
solvent such as dimethylacetamide, cresol or o-chlorophenol.

60

polystyrene, styrene/butadiene/styrene and/or styrene/ethylene-
butylene/styrene block terpolymer.

Use of Polysulfones as the Blending or Molding Polymer.

5   Polysulfones useful as the thermoplastic polymer in general may
be described as polymers containing aromatic rings which are
para-linked partly by sulfone groups and partly by dissimilar
groups such as an ether or alkyl group or a single bond. A
polysulfone does not, however, contain the carbonate [-C(O)-]

10   linkage. A polysulfone is a clear, rigid thermoplastic with a
glass transition temperature of about 180-250°C.

A common variety of polysulfone is prepared by a nucleophilic
substitution of 4,4'-dihalodiphenyl sulfone by Bisphenol-A in a

15   dipolar aprotic solvent such as dimethyl sulfoxide or 1-methyl-2-
pyrrolidinone. A fluoride or chloride may be used as the dihalide
monomer. As in the production of polycarbonate, the bisphenol is
activated to bisphenate form in a stoichiometric quantity of aqueous
base such as sodium or potassium hydroxide. However, excess water is

20   removed from the system by azeotropic distillation at 120-140°C before
the bisphenate is contacted with the dihalo monomer.

Polymerization is then carried out at 130-160°C under an inert
atmosphere to prevent oxidation of the bisphenate salt. Molecular

25   weight as high as 250,000 can be obtained in one hour, and
monofunctional halides or phenols are consequently used as chain
terminators to prevent the molecular weight of the polysulfone from
becoming so high that it is too viscous for processing. The highest
molecular weight of a Bisphenol-A polysulfone is obtained as the ratio

30   of starting monomers approaches unity, and, for useful properties,
that weight (expressed as reduced viscosity in chloroform at a
concentration of 0.2g/100mL at 25°C) is usually at least 0.4 dL/g.
Bisphenol-A polysulfone is available from Amoco Performance Products,
Inc. as Udel™ polysulfone.

35

sulfone dianhydride, 1,2,5,6-naphthalenetetracarboxylic acid
dianhydride, 2,2',3,3'-biphenyltetracarboxylic acid dianhydride,
hydroquinone bisether dianhydride, bis(3,4-dicarboxyphenyl) sulfoxide
dianhydride, and 3,4,9,10-perylene tetracarboxylic acid dianhydride.

Bisphenols useful for preparation of a polyetherimide include
those described above in connection with the preparation of
polycarbonate. Representative dinitrobisimides useful for preparation
of a polyetherimide include 1,3-bis(4-nitrophthalimido)benzene, 1,4-
bis(4-nitrophthalimido)benzene, 4,4'bis(nitrophthalimido)diphenyl
ether, 4,4'-bis(4-nitrophthalimido)diphenylmethane, 2,4-bis(4-
nitrophthalimido)toluene, and 1,6-bis(4-nitrophthalimido)hexane.

Processes for Preparing Blends of the Branched Block Ethylene
Polymers with the Blending or Modifying Polymer. Preparation of the
compositions of this invention can be accomplished by any suitable
mixing means known in the art. Typically the branched block ethylene
polymer and the thermoplastic blending or molding polymer(s), and
other components or additives which are optionally present in the
compositions of this invention, are dry blended in a tumbler or shaker
in powder or particulate form with sufficient agitation to obtain
thorough distribution thereof. If desired, the dry-blended
formulation can further be subjected to malaxation or to shearing
stresses at a temperature sufficient to cause heat plastification, for
example in an extruder with or without a vacuum. Other apparatus
which can be used in the mixing process include, for example, a roller
mill, a Henschel mixer, a ribbon blender, a Banbury mixer, or a
reciprocating screw injection molding machine.

The method of preparation of a branched block ethylene polymer
disclosed above lends itself to a preferred method of preparation of a
blend of a branched ethylene polymer with a reactive thermoplastic
polymer and optionally a blending or molding polymer. When using an
extruder for preparation of a branched block ethylene polymer, the
separate components from which it is prepared, and the blending
polymer, are fed in sequence through separate ports during a single
pass through one extruder for more convenient material handling.

Advancement to the final polymer is obtained by heating at 150-
200°C for 3-5 hours to perform cyclodehydation. When an aromatic
diamine is used, an accelerator such as triethylamine or acetic
acid may be used in a solvent such as chlorobenzene.

5

A polyimide may also be prepared by reaction of aromatic
dianhydrides with aromatic diisocyanates with the elimination of
carbon dioxide, or by reaction of a bismaleimide with a diamine.

10   A polyetherimide may be prepared by a nucleophilic substitution
reaction of a bisphenoxide salt with a dinitrobisimide, or by a
polyimide-forming reaction as described above between a diamine and an
ether-bridged dianhydride. The reaction between a bisphenoxide salt
and a dinitrobisimide may be conducted in a dipolar aprotic solvent,
· 15   such as dimethylformamide or dimethylsufoxide in combination with
toluene or chlorobenzene at about 40°C, or in N-methylpyrollidinone
with or without chlorobenzene at 80-130°C. A polyetherimide may also
be prepared by displacement of chloro or fluoro groups on a bisimide.

20   Diamines useful for preparation of a polyimide may be aliphatic
or aromatic and several useful varities include m- and p-
phenylenediamine, 2,4- and 2,6-diaminotoluene, p- and m-
xylylenediamine, 4,4'-diaminobiphenyl, 4,4'-diaminodiphenyl ether,
4,4'-diaminobenzophenone, 4,4'-diaminophenyl sulfone, 4,4'-
25   diaminodiphenyl sulfide, 4,4'-diaminodiphenylmethane, 3,3'-
dimethylbenzidine, 4,4'-isopropylidenedianiline, 1,4-bis(p-
aminophenoxy)benzene, 1,3-bis(p-aminophenoxy)benzene, hexa-, hepta,
nona-, and decamethylenediamines, 1,4-cyclohexanediamine, and bis(4-
aminocyclohexyl)methane. Representative dianhydrides useful for
30   preparation of a polyimide include pyromellitic dianhydride,
benzophenone dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane
dianhydride, 3,3',4,4'-biphenyltetracarboxylic acid dianhydride,
bis(3,4-dicarboxyphenyl) ether dianhydride, bis(3,4-dicarboxyphenyl)
thioether dianhydride, bisphenol A bisether dianhydride, 2,2-bis(3,4-
35   dicarboxylphenyl)hexafluoropropane dianhydride, 2,3,6,7-
naphthalenetetracarboxylic acid dianhydride, bis(3,4-dicarboxyphenyl)

Concerning the Incorporation of an Additional Supplemental
Impact Modifier Into Blends of the Branched Block Ethylene Polymers
with the Blending or Molding Polymer.

5   In a further embodiment of the invention, a blend of the branched
block ethylene polymer with the blending or molding thermoplastic
polymer may futher include a supplemental impact modifier. Although
the branched block ethylene polymer effectively serves as an impact
modifier when present in a composition with a blending or molding
10   polymer, better performance still may be attained in various
situations by establishing a synergy in a composition between a
branched block ethylene polymer and a supplemental impact modifier.

        Appropriate supplemental impact modifiers include, for example,
15   elastomers such as an A-B or A-B-A copolymer, a core-shell grafted
copolymer or mixtures thereof.

        An A-B or A-B-A copolymer useful as an impact modifier herein can
be either linear, branched, radial or teleblock, and can be either a
20   di-block ("A-B") copolymer, tri-block ("A-B-A") copolymer, or radial
teleblock copolymer with or without tapered sections, i.e. portions of
the polymer where the monomers alternate or are in random order close
to the point of transition between the A and B blocks.

25   The A portion is frequently prepared by polymerizing one or more
vinyl aromatic hydrocarbon monomers such as the various styrenic
monomers and substituted varieties thereof; has a weight average
molecular weight of about 4,000 to about 115,000; and has properties
characteristic of thermoplastic substances in that it has the
30   stability necessary for processing at elevated temperatures and yet
possesses good strength below the temperature at which it softens.
The B portion of the copolymer typically results from polymerizing
substituted or unsubstituted C_3-C_{10} dienes, particularly conjugated
dienes such as butadiene or isoprene; has a weight average molecular
35   weight of about 20,000 to about 450,000; and is characterized by
elastomeric properties which allow it to to absorb and dissipate an
applied stress and then regain its shape.

        To reduce oxidative and thermal instability, the A-B or A-B-A

64

Materials which are added later in the sequence are typically fed
through a downstream port in the extruder.

For example, an ethylene polymer may be fed first, followed next
5   by an ethylenically unsaturated functionalized organic compound,
followed then by a reactive thermoplastic polymer, and followed last
by the blending or molding polymer. In the alternative, a previously
prepared branched ethylene polymer may be fed first, followed next by
a reactive thermoplastic polymer, followed last by the blending or
10   molding polymer. In the alternative, a previously prepared branched
ethylene polymer may be fed together with a reactive thermoplastic
polymer, followed then by the blending or molding polymer.

Selection of the sequence in which the branched ethylene polymer
·15   reacts with the reactive thermoplastic polymer to form the branched
block ethylene polymer before the blending or molding polymer is added
to the mixer gives a product having superior properties compared to
addition of the blending polymer before or simultaneously with the
reactive thermoplastic polymer. Such a result is obtained because the
20   presence of the blending or molding polymer may act as a physical
barrier which hinders formation of the ethylenically unsaturated
functionalized organic compound into a branch, or may hinder reaction
of the reactive thermoplastic polymer with any such branched that are
formed.
25
Preparation of Articles Comprising Blends fo the Branched Block
Ethylene Polymer with the Blending or Molding Thermoplastic
Polymer(s). When softened or melted by the application of heat and/or
shear, the compositions of this invention are useful for fabrication
30   and can be formed or molded using conventional techniques such as
compression, injection molding, gas assisted injection molding,
calendering, vacuum forming, thermoforming, extrusion and/or blow
molding, alone or in combination. The compositions can also be
formed, spun or drawn into films, fibers, multi-layer laminates or
35   extruded sheets, or can be compounded with one or more organic or
inorganic substances, on any machine suitable for such purpose.

acrylonitrile; a C1-C8 alkyl acrylate such as ethyl acrylate or hexyl
acrylate; a C1-C8 alkyl methacrylate such as methyl methacrylate or
hexyl methacrylate; glycidyl methacrylate; acrylic or methacrylic
acid; and the like or a mixture of two or more thereof. The
5   preferred grafting monomers include one or more of styrene,
acrylonitrile and methyl methacrylate.

The grafting monomers may be added to the reaction mixture
simultaneously or in sequence, and, when added in sequence, layers,
10 shells or wart-like appendages can be built up around the substrate
latex, or core. The monomers can be added in various ratios to each
other although, when just two are used, they are frequently utilized
in equal amounts. A typical weight ratio for methyl
methacrylate/butadiene/styrene copolymer ("MBS" rubber) is about 60-80
·15 parts by weight substrate latex, about 10-20 parts by weight of each
of the first and second monomer shells. A preferred formulation for
an MBS rubber is one having a core built up from about 71 parts of
butadiene, about 3 parts of styrene, about 4 parts of methyl
methacrylate and about 1 part of divinyl benzene; a second phase of
20 about 11 parts of styrene; and a shell phase of about 11 parts of
methyl methacrylate and about 0.1 part of 1,3-butylene glycol
dimethacrylate, where the parts are by weight of the total
composition. A diene-based, core-shell graft copolymer elastomer and
methods for making same, as described above, are discussed in greater
25 detail in Saito, USP 3,287,443, Curfman, USP 3,657,391, and Fromuth,
USP 4,180,494.

A core-shell grafted copolymer based on an alkyl acrylate rubber
has a first phase forming an elastomeric core and a second phase
30 forming a rigid thermoplastic phase about said elastomeric core. The
elastomeric core is formed by emulsion or suspension polymerization of
monomers which consist of at least about 50 weight percent alkyl
and/or aralkyl acrylates having up to fifteen carbon atoms, and,
although longer chains may be used, the alkyls are preferably C_2-C_6,
35 most preferably butyl acrylate. The elastomeric core phase should
have a Tg of less than about 10°C, and preferably less than about -
20°C. About 0.1 to 5 weight percent of (i) a cross-linking monomer ·
which has a plurality of addition polymerizable reactive groups all of
which polymerize at substantially the same rate, such as butylene

66

copolymers used herein can also desirably be hydrogenated to reduce
the degree of unsaturation on the polymer chain and on the pendant
aromatic rings.

5   The most preferred vinyl aromatic A-B or A-B-A copolymers are
vinyl aromatic/conjugated diene block copolymers formed from styrene
and butadiene or styrene and isoprene. When the styrene/butadiene
copolymers are hydrogenated, they are frequently represented as
styrene/(ethylene/butylene) copolymer in the di-block form, or as
10   styrene/(ethylene/butylene)/styrene copolymer in the tri-block form.
When the styrene/isoprene copolymers are hydrogenated, they are
frequently represented as styrene/(ethylene/propylene) copolymer in
the di-block form, or as styrene/(ethylene/propylene)/ styrene
copolymer in the tri-block form. Vinyl aromatic/diene A-B or A-B-A
15   copolymers such as are described above are discussed in greater detail
in Holden, USP 3,265,766, Haefele, USP 3,333,024, Wald, USP 3,595,942,
and Witsiepe, USP 3,651,014, which are available commercially as the
various Kraton elastomers from Shell Chemical Company.

20   Core-shell grafted copolymer elastomers suitable for use herein
as a supplemental impact modifier are those which are based on either
a diene rubber, an alkyl acrylate rubber, or on mixtures thereof, and
have an elastomeric, or rubber, phase which is greater than about 45%
or more of the copolymer by weight. A core-shell grafted copolymer
25   based on a diene rubber contains a substrate latex, or core, which is
made by polymerizing a diene, preferably a conjugated diene, or by
copolymerizing a diene with a mono-olefin or a polar vinyl compound,
such as styrene, acrylonitrile, or an alkyl ester of an unsaturated
carboxylic acid such as methyl methacrylate. The substrate latex is
30   typically made up of about 40-85% diene, preferably a conjugated
diene, and about 15-60% of the mono-olefin or polar vinyl compound.
The elastomeric core phase should have a glass transition temperature
("Tg") of less than about 10°C, and preferably less than about -20°C.
A mixture of ethylenically unsaturated monomers is then graft
35   polymerized to the substrate latex. A variety of monomers may be used
for this grafting purpose, of which the following are exemplary:
vinyl compounds such as vinyl toluene or vinyl chloride; vinyl
aromatics such as styrene, alpha-methyl styrene or halogenated
styrene; acrylonitrile, methacrylonitrile or alpha-halogenated

65

chain, hydrocarbon backbone ("olefinic elastomers"), which may be
prepared predominantly from various mono- or dialkenyl monomers and
may be grafted with one or more styrenic monomers. Representative
examples of a few olefinic elastomers which illustrate the variation
5 in the known substances which would suffice for such purpose are as
follows: butyl rubber; chlorinated polyethylene rubber;
chlorosulfonated polyethylene rubber; an olefin polymer or copolymer
such as ethylene/propylene copolymer, ethylene/styrene copolymer or
ethylene/propylene/diene copolymer, which may be grafted with one or
10 more styrenic monomers; neoprene rubber; nitrile rubber;
polybutadiene and polyisoprene.

An example of a preferred olefinic elastomer is a copolymer
prepared from (i) at least one olefin monomer such as ethylene,
· 15 propylene, isopropylene, butylene or isobutylene, or at least one
conjugated diene such as butadiene, and the like, or mixtures thereof;
and (ii) an ethylenically unsaturated monomer carrying an epoxide
group (for example, glycidyl methacrylate), and, optionally, (iii) an
ethylenically unsaturated monomer which does not carry an epoxide
20 group (for example, vinyl acetate).

When the supplemental impact modifier is employed, it will
advantageously be present in an amount (in parts by weight of the
total blend composition) of at least about 1 part, preferably at least
25 about 5 parts, more preferably at least about 10 parts, and most
preferably at least about 15 parts. The supplemental impact modifier
will typically be present in an amount of not more than about 50
parts, advantageously not more than about 40 parts, preferably not
more than about 30 parts, and more preferably not more than about 25
30 parts.

When the supplemental impact modifier is employed in conjunction
with blends of a thermoplastic (such as polycarbonate) with a branched
block ethylene polymer having a polyester as the reactive
· 35 thermoplastic polymer component (c), the supplemental impact modifier
will be present in such blend in an amount (in parts by weight of the
total blend composition) of at least about 0.1 parts, advantageously
at least about 0.5 parts, preferably at least about 1 parts, and more
preferably at least about 3 parts; and yet not more than about about

diacrylate, and (ii) a graft-linking monomer which has a plurality of
addition polymerizable reactive groups some of which polymerize at
substantially different rates than others, such as diallyl maleate, is
typically polymerized as part of the elastomeric core.

5

The rigid thermoplastic phase of the acrylate rubber is formed on
the surface of the elastomeric core using suspension or emulsion
polymerization techniques. The monomers necessary to create this
phase together with necessary initiators are added directly to the
10   reaction mixture in which the elastomeric core is formed, and
polymerization proceeds until the supply of monomers is substantially
exhausted. Ethylenically unsaturated monomers such as glycidyl
methacrylate, or an alkyl ester of an unsaturated carboxylic acid, for
example a C_1-C_8 alkyl acrylate like methyl acrylate, hydroxy ethyl
15   acrylate or hexyl acrylate, or a C_1-C_8 alkyl methacrylate such as
methyl methacrylate or hexyl methacrylate, or mixtures of any of the
foregoing, are some of the vinyl monomers which can be used for this
purpose. Either thermal or redox initiator systems can be used.
Because of the presence of the graft linking agents on the surface of
20   the elastomeric core, a portion of the chains which make up the rigid
thermoplastic phase are chemically bonded to the elastomeric core. It
is preferred that there be at least about 20% bonding of the rigid
thermoplastic phase to the elastomeric core.

25   A preferred acrylate rubber is made up of more than about 45% to
about 95% by weight of an elastomeric core and about 60% to about 5%
of a rigid thermoplastic phase. The elastomeric core can be
polymerized from about 75% to about 99.8% by weight C_1-C_6 acrylate,
preferably n-butyl acrylate. The rigid thermoplastic phase can be
30   polymerized from at least 50% by weight of C_1-C_8 alkyl methacrylate,
preferably methyl methacrylate. Acrylate rubbers and methods for
making same, as described above, are discussed in greater detail in
Owens, USP 3,808,180 and Witman, USP 4,299,928. Various diene-based
and acrylate-based core-shell grafted copolymers are available
35   commercially from Rohm & Haas as the Acryloid™ or Paraloid™
elastomers.

Other supplemental impact modifiers or elastomers useful in the
compositions of this invention are those based generally on a long-
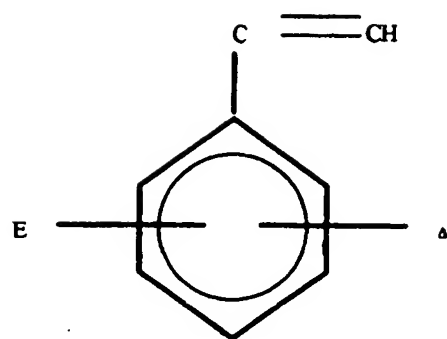
25 parts, advantageously not more than about 20 parts, preferably not
more than about 15 parts, and more preferably not more than about 10
parts.

5   Concerning the Use of a Styrenic Copolymer as an Additional Component
     of Blends of the Branched Block Ethylene Polymer with the Blending or
     Molding Thermoplastic Polymer.

        In the embodiment of the invention which is a blend of the
10   branched block ethylene polymer with a blending or molding
     thermoplastic polymer, such blend may further comprise a styrenic
     copolymer. Such styrenic copolymers have found particular utility in
     blends of the branched block ethylene polymer in which the reactive
     thermoplastic polymer is a polyester.

15

        Suitable styrenic copolymers will be prepared from one or more
     styrenic monomers and one or more ethylenically unsaturated monomers
     copolymerizable with a styrenic monomer. The styrenic copolymer may
     be a random, alternate, block or grafted copolymer, and a mixture of
20   more than one styrenic copolymer may be used as well.


        Styrenic monomers of particular interest for use in preparation
     of a styrenic copolymer, in addition to styrene itself, include one or
25   more of the substituted styrenes or vinyl aromatic compounds described
     by the following formula [it being understood that a reference to
     "styrene" as a comonomer in component (c) is to be read as a reference
     to any of the styrenic or vinyl aromatic monomers described herein or
     any others of like kind]:

natural rubber, chlorinated rubber, 1,2-hexadiene, methyl-1,3-
pentadiene, 2,3-dimethyl-1,3-1,3-pentadiene, 2-methyl-3-ethyl-1,3-
butadiene, 2-ethyl-1,3-pentadiene, 1,3- and 2,4-hexadienes, chloro-
and bromo-substituted butadienes such as dichlorobutadiene,

5   bromobutadiene, chloroprene and dibromobutadiene, and
butadiene/isoprene and isoprene/isobutylene copolymers; 1,3-
divinylbenzene; 2-phenyl propene; a C_2-C_{10} alkylene compound
including halo-substituted derivatives thereof such as vinyl or
vinylidine chloride; the alpha,beta-ethylenically unsaturated

10 carboxylic acids, such as acrylic acid, methacrylic acid, maleic acid,
succinic acid, acotinic acid and itaconic acid, and their anhydrides
and C_1-C_10 alkyl, aminoalkyl and hydroxyalkyl esters and amides, such
•   as alkyl acrylates and methacrylates such as methyl acrylate, propyl
acrylate, butyl acrylate, octyl acrylate, methyl alpha-chloro

‚15 acrylate, methyl, ethyl or isobutyl methacrylate, hydroxyethyl and
hydroxypropyl acrylates, aminoethyl acrylate and glycidyl
methacrylate; maleic anhydride; an alkyl or aryl maleate or fumarate
such as diethylchloromaleate or diethyl fumarate; an aliphatic or
aromatic maleimide, such as N-phenyl maleimide, including the reaction

20 product of a C_1-C_{10} alkyl or C_6-C_{14} aryl primary amine and maleic
anhydride; methacrylamide, acrylamide or N.N-diethyl acrylamide;
vinyl ketones such as methyl vinyl ketone or methyl isopropenyl
ketone; vinyl or allyl acetate and higher alkyl or aryl vinyl or
allyl esters; vinyl alcohols; vinyl ethers such as C_1-C_6 alkyl vinyl

25 ether and their alkyl-substituted halo derivatives; vinyl pyridines;
vinyl furans; vinyl aldehydes such as acrolein or crotonaldehyde;
vinyl carbazole; vinyl pyrrolidone; N-vinylphthalimide; and an
oxazoline compound includes those of the general formula, where each J
is independently hydrogen, halogen, a C_1-C_{10} alkyl radical or a C_6-C_{14}

30 aryl radical; and the like:

72

wherein each A is independently hydrogen, a C_1-C_6 alkyl radical or a
halogen atom such as chlorine or bromine; and each E is independently
hydrogen, a C_1-C_{10} alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl,
alkaryl, aralkyl or alkoxy radical, a halogen atom such as chlorine or
5   bromine, or two E's may be joined to form a naphthalene structure.
Representative examples of suitable styrenic monomers, in addition to
styrene itself, include one or more of the following: ring-substituted
alkyl styrenes, e.g. vinyl toluene, o-ethylstyrene, p-ethylstyrene,
ar-(t-butyl)styrene, 2,4-dimethylstyrene; ring-substituted
10   halostyrenes, e.g., o-chlorostyrene, p-chlorostyrene, o-bromostyrene,
2,4-dichlorostyrene; ring-alkyl, ring-halo-substituted styrenes, e.g.
2-chloro-4-methylstyrene and 2,6-dichloro-4-methylstyrene; ar-methoxy
styrene, vinyl naphthalene or anthracene, p-diisopropenylbenzene,
divinylbenzene, vinylxylene, alpha-methylstyrene, and alpha-
15   methylvinyltoluene.

Ethylenically unsaturated monomers of particular interest for
copolymerization with a styrenic monomer include one or more of those
described by the formula:
20

$$D--CH==C(D)--(CH_2)_n--G,$$
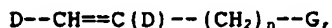
wherein each D independently represents a substituent selected from
the group consisting of hydrogen, halogen (such as fluorine, chlorine
25   or bromine), C_1-C_6 alkyl or alkoxy, or taken together represent an
anhydride linkage; G is hydrogen, vinyl, C_1-C_{12} alkyl, cycloalkyl,
alkenyl, cycloalkenyl, alkaryl, arylalkyl, alkoxy, aryloxy, ketoxy,
halogen (such as fluorine, chlorine or bromine), cyano or pyridyl; and
n is 0-9.
30

Representative examples of ethylenically unsaturated monomers
copolymerizable with a styrenic monomer are those which bear a polar
or electronegative group and include one or more of the following: a
vinyl nitrile compound such as acrylonitrile, methacrylonitrile,
35   ethacrylonitrile, alphachloroacrylonitrile and fumaronitrile; a diene
such as butadiene, isoprene, isobutylene, piperylene, cyclopentadiene,

$$\overline{C\,(J2)==C\,(J)--C==N--C\,(J2)--}$$
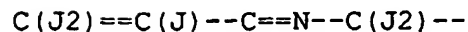
Examples of preferred styrenic copolymers are vinyl aromatic/vinyl nitrile copolymers such as styrene/acrylonitrile
5 copolymer ("SAN"), styrene/maleic anhydride copolymer, styrene/glycidyl methacrylate copolymer, aryl maleimimde/vinyl nitrile/diene/styrenic copolymer, strene/alkyl methacrylate copolymer, styrene/alkyl methacrylate/glydicyl methacrylate copolymer, styrene/butyl acrylate copolymer, methyl
10 methacryalte/acrylonitrile/butadiene/styrene copolymer, or a rubber-modified vinyl aromatic/vinyl nitrile copolymer such as an ABS, AES or ASA copolymer.

ABS (acrylonitrile/butadiene/styrene copolymer) is an
15 elastomeric-thermoplastic composite in which vinyl aromatic/vinyl nitrile copolymer is grafted onto a polybutadiene substrate latex. The polybutadiene forms particles of rubber – the rubber modifier or elastomeric component – which are dispersed as a discrete phase in a thermoplastic matrix formed by random vinyl aromatic/vinyl nitrile
20 copolymer. Typically, vinyl aromatic/vinyl nitrile copolymer is both occluded in and grafted to the particles of rubber. AES (acrylonitrile/EPDM/styrene) copolymer is a styrenic copolymer which is obtained when vinyl aromatic/vinyl nitrile copolymer is rubber-modified by grafting vinyl aromatic/vinyl nitrile copolymer to a
25 substrate made up of an EPDM (ethylene/propylene/non-conjugated diene) rubber. AES copolymers are discussed in greater detail in Henton, USP 4,766,175. A vinyl aromatic/vinyl nitrile copolymer can also be crosslinked to an alkyl acrylate elastomer to form a rubber-modified styrenic copolymer, as in the case of an ASA
30 (acrylonitrile/styrene/acrylate) copolymer, which is discussed in greater detail in Yu, USP 3,944,631.

74

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invention. Preferably, however, the melt flow viscosity of the
styrenic copolymer as determined by ASTM D-1238-65T(1) is from about
0.01 to about 10, more preferably from about 0.1 to about about 5, and
most preferably from about 2 to about 3, deciliters per minute. When

5   the ethylenically unsaturated monomer possesses a polar group, the
polar group typically has a group moment of about 1.4 to 4.4 Debye
units, although values outside such ranges are permitted as well. A
styrenic copolymer may be made by an emulsion, suspension or mass
(bulk) method.

10

Methods for making ABS or other styrenic copolymers, as
described above, are discussed in greater detail in Childers, USP
2,820,773, Calvert, USP 3,238,275, Carrock, USP 3,515,692, Ackerman,
USP 4,151,128, Kruse, USP 4,187,260, Simon, USP 4,252,911 Weber, USP

15   4,526,926, Rudd, USP 4,163,762 and Weber, USP 4,624,986.

The styrenic copolymer (when present) in the blends of the
blending or molding thermoplastic polymer and the branched block
ethylene polymer, will be present in an amount (in parts by weight

20   based on the total weight of the blend composition) of at least about
5 parts, advantageously at least about 10 parts, preferably at least
about 15 parts, and more preferably at least about 20 parts, and yet
not more than about about 75 parts, advantageously not more than about
55 parts, preferably not more than about 50 parts, and more preferably

25   not more than about 45 parts.

Concerning the Presence of a Flow Modifier to Blends of the
Branched Block Ethylene Polymer with a Blending or Molding
Thermoplastic Polymer.

30   Blends of the branched block ethylene polymer with a blending or
molding thermoplastic polymer may advantageously further include a
flow modifier. Exemplary flow modifiers are polyamides and/or
polyolefins.

The monomers copolymerized to form a styrenic copolymer may each
be used in virtually any amount from 1 to 99 weight percent, but a
styrenic copolymer will typically contain at least about 15 percent by
5   weight, preferably at least about 35 percent by weight, and more
preferably at least about 60 percent by weight of a styrenic monomer,
with the balance being made up of one or more copolymerizable
ethylenically unsaturated monomers. When rubber-modified, a styrenic
copolymer will typically contain at least about 15 percent by weight,
10   preferably at least about 25 percent by weight, and more preferably at
least about 35 percent by weight of a styrenic monomer, with the
balance being made up of one or more copolymerizable ethylenically
unsaturated monomers.

15   The elastomeric phase of a rubber-modified styrenic copolymer as
employed in the compositions of this invention is up to about 45
percent, preferably about 5 to 40 percent, more preferably about 10 to
35 percent, by weight of the copolymer. The preferred elastomeric
phase exhibits a glass transition temperature (Tg) generally less than
20   0°C, more preferably less than -30°C, and most preferably from about -
110°C to about -50°C as determined by ASTM D-746-52T or -56T. The
elastomeric phase advantageously has an average particle size of about
10 microns or less, preferably in the range from about 0.05 to about 5
microns, and more preferably in the range from about 0.1 to about 0.3
25   microns, and typically exhibits an intrinsic viscosity, as determined
at 25°C in toluene, of about 0.1 to about 5. In addition to the
aforementioned monomeric components, the elastomeric phase may also
contain relatively small amounts, usually less than about 2 weight
percent based on the rubber, of a crosslinking agent such a
30   divinylbenzene, diallylmaleate, ethylene glycol dimethacrylate and the
like provided that such crosslinking does not eliminate the desired
elastomeric character of rubber.

The molecular weight of a styrenic copolymer is not particularly
35   critical so long as its melt flow viscosity is such that it can be
melt blended with the other components of the compositions of this

advantageously not more than about 98 parts, and preferably not
more than about 95 parts;

(c)   Styrenic Copolymer (when present): at least about 5 parts,
        advantageously at least about 10 parts, preferably at least
5   about 15 parts, and more preferably at least about 20 parts, and
        yet not more than about about 75 parts, advantageously not more
        than about 55 parts, preferably not more than about 50 parts,
        and more preferably not more than about 45 parts;

(d)   Supplemental Impact Modifier (when present): at least about 0.1
10   parts, advantageously at least about 0.5 parts, preferably at
        least about 1 parts, and more preferably at least about 3 parts,
        and yet not more than about about 25 parts, advantageously not
        more than about 20 parts, preferably not more than about 15
        parts, and more preferably not more than about 10 parts; and

15 (e) Flow Modifier Resin (when present): at least about 5 parts,
        advantageously at least about 10 parts, preferably at least
        about 15 parts, and more preferably at least about 20 parts, and
        yet not more than about about 75 parts, advantageously not more
        than about 55 parts, preferably not more than about 50 parts,
20   and more preferably not more than about 45 parts.

Particular Embodiment Wherein the Reactive Thermoplastic Polymer is a
Polycaprolactone.

        In one particular embodiment of the invention, branched block
        ethylene polymer will comprise a branched block ethylene polymer,
25 wherein the reactive thermoplastic polymer is a polycaprylactone.
        Such compositions will find utility in combination with polycarbonate
        and a homogeneous ethylene polymer as the blending or molding polymers
        and a styrene-acrylonitrile grafted ethylene-propylene-diene rubber as
        the supplemental impact modifier. Such blends will comprise from
30 0.001 - 50 weight percent of the branched block ethylene polymer, 0.01
        - 50 weight percent of the homogeneous ethylene polymer, 50-99.99

Polyamides useful as flow modifiers are as described above with respect to amine-functionalized polymers useful as the reactive thermoplastic polymer of subcomponent (c) of the branched block ethylene polymers of the invention. Polyolefins useful as flow modifiers are as described above with respect to possible compositions of the thermoplastic blending or molding polymer.

The flow modifier resin (when present) in the blends of the blending or molding thermoplastic polymer and the branched block ethylene polymer, will be present in an amount (in parts by weight based on the total weight of the blend composition) of at least about 5 parts, advantageously at least about 10 parts, preferably at least about 15 parts, and more preferably at least about 20 parts. Likewise, the flow modifier resin will be present in an amount of not more than about about 75 parts, advantageously not more than about 55 parts, preferably not more than about 50 parts, and more preferably not more than about 45 parts.

Preferred Compositions Utilizing Branched Block Ethylene Polymers in Which the Reaction Thermoplastic Polymer of Subcomponent (c) is a Polyester:

Preferred compositions utilizing branched block ethylene polymers in which the reaction thermoplastic polymer of subcomponent (c) is a polyester will comprise the following:

(a)   Branched Block Ethylene Polymer: at least about 1 parts, advantageously at least about 2 parts, and preferably at least about 5 parts, and yet not more than about about 40 parts, advantageously not more than about 30 parts, and preferably not more than about 20 parts;

(b)   Thermoplastic Blend or Molding Polymer: at least about 60 parts, advantageously at least about 70 parts, and preferably at least about 80 parts, and yet not more than about about 99 parts,

acid; alumina trihydrate; ammonium fluoroborate; molybdenum oxide;
halogenated hydrocarbons such as hexabromocyclodecane;
decabromomdiphenyl oxide; 1,2-bis(2,4,6-tribromophenoxy) ethane;
halogenated carbonate oligomers such as those prepared from

5 tetrabromobisphenol-A; halogenated epoxy resins such as brominated
glycidyl ethers; tetrabromo phthalic anhydride; fluorinated olefin
polymers or copolymers such as poly(tetrafluoroethylene);
octabromodiphenyl oxide; ammonium bromide; isopropyl di(4-amino
benzoyl) isostearoyl titanate; and metal salts of aromatic sulfur

10 compounds such as sulfates, bisulfates, sulfonates, sulfonamides and
sulfimides; other alkali metal and alkaline earth metal salts of
sulfur, phosphorus and nitrogen compounds; and others as set forth in
Laughner, USP 4,786,686; and the like, and mixtures thereof. A
preferred flame retardant additive is antimony trioxide (Sb_2O_3). When

15 a flame retardant is used in the compositions of this invention, it is
typically used in an amount of up to about 15 percent, advantageously
from about 0.01 to 15 percent, preferably from about 0.1 to 10 percent
and more preferably from about 0.5 to 5 percent, by weight of the
total composition.

20

A variety of additives are optionally advantageously used in the
compositions of this invention for other purposes such as the
following: antimicrobial agents such as organometallics,
isothtazolones, organosulfurs and mercaptans; antioxidants such as

25 phenolics, secondary amines, phophites and thioesters; antistatic
agents such as quaternary ammonium compounds, amines, and ethoxylated,
propoxylated or glycerol compounds; fillers and reinforcing agents
such as talc, clay, mica, silica, quartz, kaolin, aluminum nitride,
TiO_2, calcium sulfate, B_2O_3, alumina, glass flakes, beads, whiskers or

30 filaments, nickel powder and metal or graphite fibers; hydrolytic
stabilizers; lubricants such as fatty acids, fatty alcohols, esters,
fatty amides, metallic stearates, paraffinic and microcrystalline
waxes, silicones and orthophosphoric acid esters; mold release agents
such as fine-particle or powdered solids, soaps, waxes, silicones,

35 polyglycols and complex esters such as trimethylolpropane tristearate
or pentaerythritol tetrastearate; pigments, dyes and colorants;

80

weight percent polycarbonate, and 0.001 - 10 weight percent of the styrene-acrylonitrile grafted ethylene-propylene-diene rubber.

Such compositions have good melt processability and toughness, making them useful for profile extrusion, injectin molding
5   applicaitons for automotive applications, computer and business equipment, communication devices, and other thin wall injection molding applications.

Concerning the Presence of Additives to the Branched Block Ethylene Polymers and/or to the Blends of the Branched Block Ethylene Polymers
10   with an Additional Blending or Molding Polymer:

A variety of additives are optionally advantageously employed to promote flame retardance or ignition resistance in the compositions of this invention. Representative examples thereof include the oxides
15   and halides of the metals of Groups IVA and VA of the periodic table such as the oxides and halides of antimony, bismuth, arsenic, tin and lead such as antimony oxide, antimony chloride, antimony oxychloride, stannic oxide, stannic chloride and arsenous oxide; the organic and inorganic compounds of phosphorous, nitrogen, boron and sulfur such as
20   aromatic phosphates and phosphonates (including halogenated derivatives thereof), alkyl acid phosphates, tributoxyethyl phosphate, 1,3-dichloro-2-propanol phosphate, 3,9-tribromoneopentoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5)undecane-3,9-dioxide, phosphine oxides, ammonium phosphate, zinc borate, thiourea, urea, ammonium
25   sulfamate, ammonium polyphosphoric acid and stannic sulfide; the oxides, halides and hydrates of other metals such as titanium, vanadium, chromium and magnesium such as titanium dioxide, chromic bromide, zirconium oxide, ammonium molybdate and stannous oxide hydrate; antimony compounds such as antimony phosphate, sodium
30   antimonate, $KSb(OH)_6$, NH_4SbF_6 and SbS_3; antimonic esters of inorganic acids, cyclic alkyl antimonite esters and aryl antimonic acid compounds such as potassium antimony tartrate, the antimony salt of caproic acid, $Sb(OCH_2CH_3)$, $Sb[OCH(CH_3)CH_2CH_3]_3$, antimony polyethylene glycorate, pentaerythritol antimonite and triphenyl antimony; boric

preferably at least about 1 and even more preferably at least about 10 percent by weight.

Examples

5

The following examples are offered to illustrate but not limit the invention. Percentages, ratios and parts are by weight unless stated otherwise. Examples of the invention (Ex.) are designated numerically, while comparative samples (C.S.), which are not examples

10   of the invention, are designated alphabetically.

To illustrate the practice of this invention, examples of several preferred embodiments are set forth below, however, these examples are not meant in any manner to restrict the scope of this

15   invention. Some of the particularly desirable features of this invention may be seen by contrasting the characteristics of the Examples with those of various controlled formulations (Comparative Samples) which do not possess the features of, and are not therefore embodiments of, this invention.

20

Unless indicated otherwise, for Examples 1-7, the branched block ethylene polymer contained in the compositions of the Examples is prepared by dry blending Nylon 6 (having a weight average molecular weight of 22,000 and a melt index of 7), and a linear or substantially

25   linear ethylene polymer (containing a 1 weight percent maleic anhydride branch) in amounts, respectively, as shown below. The maleic anhydride branch is formed on the linear or substantially linear ethylene polymer in an amount of 1 weight percent, based on the weight of the branched linear or substantially linear ethylene

30   polymer, using a peroxide initiator. The dry blend of Nylon 6 and branched linear or substantially linear ethylene polymer is then melt mixed in a 30 mm Werner & Pfleiderer extruder to cause the Nylon 6 to react with the maleic anhydride branch and add as the final block to form a branched block ethylene polymer. Conditions used in such

35   reactive extrusion are: zone temperatures of 150, 200, 250, 250 and 250°C; 250 rpm; 70-85 percent torque; and a 30 second residence time.

82

plasticizers such as esters of dibasic acids (or their anhydrides) with monohydric alcohols such as o-phthalates, adipates and benzoates; heat stabilizers such as organotin mercaptides, an octyl ester of thioglycolic acid and a barium or cadmium carboxyalte; ultraviolet

5   light stabilizers such as a hindered amine, an o-hydroxy-phenylbenzotriazole, a 2-hydroxy,4-alkoxybenzophenone, a salicylate, a cyanoacrylate, a nickel chelate and a benzylidene malonate and oxalanilide. A preferred hindered phenolic antioxidant is Irganox™ 1076 antioxidant, available from Ciba-Geigy Corp. Such additives, if

10   used, typically do not exceed 45 percent by weight of the total composition, and are advantageously from about 0.001 to 15 percent, preferably from about 0.01 to 10 percent and more preferably from about 0.1 to 10 percent, by weight of the total composition.

15   In the case of blends of the branched block ethylene polymers with an additional modifying or blending polymer, the polymer blend may likewise optionally include other additives, such as fillers, colorants, antioxidants, antistats, slip agents, tackifiers, fragrances, and the like.

20

Concerning the Use of the Branched Block Ethylene Polymers to Enhance Service Temperature. The branched block ethylene polymers of the invention have a relatively softer segment of ethylene polymer and a relatively harder segment of reactive thermoplastic polymer, which

25   will preferably be an engineering thermoplastic. The presence of the harder engineering thermoplastic segment serves to extend the upper service temperature of the ethylene polymer. In this embodiment, the engineering thermoplastic impact modifiers are preferably present in amounts less than about 50, more preferably less than about 40, most

30   preferably less than about 30, even more preferably less than about 20 percent by weight based on total weight of the branched block ethylene polymer of the invention. At these amounts, the engineering thermoplastic is observed to extend the range of temperatures in which the branched block ethylene polymer is serviceable (does not melt or

35   deform undesirably). The amount of ethylene copolymer is preferably at least about 0.01, more preferably at least about 0.1, most

81

"EP" is the weight percent of linear or substantially linear ethylene polymer present in the blended composition, whether the ethylene polymer is unbranched, branched or formed into a branched

5   block ethylene polymer.

Nylon 6 is a 7 melt index, 22,000 molecular weight polyamide (Capron 8207) commercially available from Allied Signal.

10   EG8200gMAH - A polyolefin elastomer having an I_2 of 5 g/10 min. grafted with 1 wt. % maleic anhydride

ENGAGE[*] 8150 - A polyolefin elastomer having an I_2 of 0.5 g/10 min., commercially available from The Dow Chemical Company.

15

The following tests of physical and mechanical properties are performed on Examples 1-5 and Controls A-C, and the results of these tests are also shown in Table I:

Impact resistance ("Izod") is measured by the Izod test

20   according to ASTM Designation D 256-84 (Method A) at 25°C. The notch is 10 mils (0.254 mm) in radius. Izod results are reported in ft-lb/in.

Impact resistance ("Weldline") is also measured by the Izod test according to ASTM Designation D 256-84 (Method A) at 25°C, but with

25   respect to a sample which is formed with a butt weld in a double gated mold. The sample is unnotched, and it is placed in the vise so that the weld is 1 mm above the top surface of the vise jaws. Weldline results are also reported in ft-lb/in, except as to Example 5 where "N.B." indicates that the sample did not break.

30   The dart drop impact test ("Dart Drop") is performed at 23°C by dropping a 100 pound weight which carries a ½" dart onto a circular test sample which is 1/8" thick. The weighted dart falls freely on a slotted track and impacts the sample, which is secured in position in the path of descent on an aluminum cast base with a 0.640 inch hole to

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[*] Trademark of The Dow Chemical Company

The branched block ethylene polymer is passed through an ice water bath, chopped into granules and collected for blending with a polyolefin resin.

5   Blend compositions are prepared by mixing the dry components of each on a paint shaker for 5 minutes, and then feeding the dry-blended formulation to the Werner & Pfleiderer extruder under the same conditions used to prepare the branched block ethylene polymer, except that the zone temperatures are 150, 200, 280, 280 and 280°C. The

10   extrudate is again cooled in the form of strands and comminuted as pellets. The pellets are dried in an air draft oven for 3 hours at 120°C, and are then used to prepare test specimens on a 70 ton Arburg molding machine on which the barrel temperature is 200°C (feed), 250°C, 250°C and 255°C (nozzel), the mold temperature is 80°F, and the

15   screw speed is 120 rpm.

       "Polypropylene" is Profax™ 6323 polypropylene from Himont;

       "HDPE" is high density polyethylene having a density of about

20   0.96 g/cm^3 and an I_2 melt index (according to ASTM D 1238) of about 10 g/10 min.;

       "POE" is an unbranched substantially linear ethylene polymer, as described above;

25   "POE-b-MAH" is a substantially linear ethylene polymer containing a maleic anhydride branch, as described above;

       "B/BEP I" is a branched block ethylene polymer prepared from 70 weight percent substantially linear ethylene polymer containing a

30   maleic anhydride branch and 30 weight percent Nylon 6;

       "B/BEP II" is a branched block ethylene polymer prepared from (i) 80 weight percent Tafmer™ P-0180 ethylene/propylene copolymer, a linear homogeneous ethylene polymer from Mitsui Petrochemical which

35   has a density of 0.869 g/cm^3, a melt index (I_2) of 4 and a maleic anhydride branch; and (ii) 20 weight percent Nylon 6; and

SPECIFIC EMBODIMENTS

Sample Preparation

All samples were prepared by feeding polymer into a Werner-
Pfleiderer ZSK-53/5L co-rotating twin screw extruder. After the
polymer was fed into the extruder, a mixture of maleic anhydride
(MAH)/methyl ethyl ketone (MEK)/LUPERSOL 130 (Initiator) at a weight
ratio of 1:1:0.032, respectively, was fed into the end of Zone 1 of
the extruder through an injection nozzle by a metering pump. LUPERSOL
130 is 2,5-di(t-butyl peroxy)hexyne-3 manufactured and sold by
Atochem. The extruder was maintained at a vacuum level of greater
than or equal to 26 inches of mercury to facilitate devolatization of
solvent, unreacted MAH and other contaminates.

Attane® resin is a ULDPE ethylene/1-octene resin manufactured
and sold by The Dow Chemical Company. Dowlex® resin is a LLDPE
ethylene/1-octene resin manufactured and sold by The Dow Chemical
Company. Tafmer® P-0180 resin is an ethylene/propylene copolymer
resin manufactured and sold by Mitsui Petrochemical.

The following materials are used:

ADMER QF 500A, a polypropylene grafted with 1.5 wt % MAH and
manufactured and sold by Mitsui Petrochemical; the grafted polymer had
a melt index of 3.0 g/10 min. at 230 C and a density of 0.900 g/cm^3.

Primacor® 3460, a copolymer of ethylene and acrylic acid
manufactured and sold by The Dow Chemical Company; this material
contained 9.7 wt % acrylic acid monomer and had a melt index of 20
g/10 min.

Graft-modified homogeneous ethylene polymer; this material
contained 1.3 wt % MAH, had a melt index of 0.25 g/10 min., and a
density of 0.870 g/cm^3.

Profax® 6524, a polypropylene manufactured and sold by Himont;
it had a melt index of 4 g/10 min. at 230 C and a density of 0.9
g/cm^3.

accept the dart after it impacts the sample. The instrument is a
Dynatup Model 8250. The sample fails if it shows a crack or
perforation on the side on which impact did not occur. The results
are either pass (no break or perforation by the dart at the point of
5   impact) or fail (material exhibits crack or perforation) when the dart
has developed a particular amount of energy by falling from the
necessary height on the track, as indicated thereon, to develop such
energy. The value recorded in Table I is either "pass" or the
greatest amount of energy a sample could accept without failing,
10   expressed in in-lb.

      Deflection temperature under load ("D.T.U.L.") is measured in
accordance with ASTM Designation D 648-82 at 66 psi. Results are
reported in °C.

      Flexural modulus ("F. Modulus") is determined according to ASTM
15   D 790. Results are reported in psi.

      Unless indicated to the contrary, the substantially linear
ethylene polymers used in the examples are prepared in accordance with
the techniques set forth in USP 5,272,236 via a solution
20   polymerization process utilizing a $[((CH_3)_4C_5))-(CH_3)_2$ Si-N-(t-
$C_4H_9)]TI(CH_3)_2$ organometallic catalyst activated with tris
(perfluorophenyl)borane. Unless indicated to the contrary, all parts
and percentages are by weight, total weight basis. Unless indicated
to the contrary, the following test procedures are utilized:

25

1.	Notched IZOD Impact (ft-lb/in)	ASTM D-256 (at 23 C, 0 C, -18 C, -29 C and -40 C)
2.	Tensile (psi)	ASTM D-638
3.	Yield (psi)	ASTM D-638
4.	Elongation (%)	ASTM D-638
5.	Whiteness Index (WI)	ASTM E-313
6.	Yellowness Index (YI)	ASTM E-313
7.	Particle Size (microns)	Electron micrographs of microtomed molded test samples ASTM D-3763-86
8.	Dynatup	ASTM D-3763-86 (at -29 C)

85

Maleic anhydride grafted ethylene 1-octene copolymer (ITP-g-MAH)
prepared by grafting maleic anhydride to ethylene-octene copolymer by
reactive extrusion was used in this study. The ethylene-octene
copolymer used to make the ITP-g-MAH was a copolymer made in solution
5 polymerization process from a constrained geometry single site
catalyst. The final graft copolymer (lot XUR-1567-48562-D4) had a
melt index of approximately 0.5 g/10 min, density of 0.87 g/cc, and
MAH content of 1 weight percent. (1%MAH-g-ITP).

Polybutyleneterephthalate (PBT) was Celanex 2002 from Celanese
10 (0.9 IV)

Acrylic copolymer consisting of methylmethacrylate-
butylacrylate-glycidyl methacrylate (MMA/GMA), 90:8:2 ratio by weight.

Test Methods:

15 The dynamic mechanical properties of the samples were studied
using Rheometrics Solid analyzer RSA-II. The test sample were
prepared in the form of thin films(about 15-20 mil thickness). The
sample was measured over a range temperature range from -120°C to
highest possible temperature at which the sample either melted or
20 deformed excessively. The measurement were conducted at the frequency
of 10 rad/s and at 7.0×10^{-4} strain.

Tensile properties were tested on an Instron Series IX Automated
Testing System 1.04. Machine parameters of test are: Sample rate
25 18.21 pts/sec; Crosshead speed: 2.00 in/min; Full Scale Load Range:
10.00(lbs); Humidity: 50%; Temperature: 73°F.

Example 1

The composition was produced by dry blending/mixing ITP-g-MAH
30 (1400 g) and PBT (600 g) and subsequently melt blending using a 30 mm
Werner & Pfleiderer twin screw extruder (250 RPM, feed rate to give
70-85% torque, and five barrel zone temperatures set at 150, 200, 250,
250, 250°C). Extrudate was pelletized using a Conair strand chopper.
The results in Figure 1 indicate that MAH-g-ITP/PBT blend has higher
35 service temperature than control samples, ITP-g-MAH or ITP/PBT blend.
Using dynamic mechanical analysis (solid state, extension), both

The graft-modified homogeneous ethylene polymer (referred to below as INSITE^{TM} Technology polymer or ITP) was prepared according to the procedure described in USP 4,950,541. The polymer components were dry mixed at a certain weight ratio, and were then fed into a Werner-Pfleiderer ZSK-30 twin-screw extruder operated at about 210 C. The blends were made in one extrusion pass.

Injection molded samples were prepared using a 50 ton Negri-Bossi Injection Molder operated with a barrel temperature between 200 and 250 C, a barrel pressure of 40 bars, cooling mold temperature of 85 F (29 C), and a residence time in the cooling mold of about 12 seconds. The samples were formed into 2.5" x 6.5" x 0.075" plaques.

The flex modulus and IZOD impact properties (at room temperature and -30 C) were measured for each of the samples in Table 8. These properties are important in many applications, e.g., automobile parts. The properties were measured according to ASTM D-790 and D-256, respectively.

Ethylene-propylene diene elastomer functionalized with maleic anhydride and sold by Uniroyal Chemical (Product designated - ROYALTUF 465A).

Ethylene-propylene elastomer functionalized with maleic anhydride and sold by Exxon Chemical (Product designated -Exxelor VA 1801).

An ethylene-propylene elastomer (Tafmer P-0180 from Mitsui) graft modified with maleic anhydride as described above.

Nylon 1000-1 is a low M_w Nylon 6,6 from Hoechst-Celanese used for injection molding

Nylon 1200-1 is a high M_w Nylon 6,6 from Hoechst-Celanese used for extrusion

granules and collected for final blending with the specified
polyolefin matrix resin

Figures 4 and 5 graphically compare the rheological and Tan
5   Delta properties at shear rates from 0.1 rads/sec to 100 rads/sec of a
substantially linear ethylene elastomer, a maleic anhydride grafted
substantially linear ethylene elastomer and a polyamide modified
substantially linear ethylene elastomer. Figures 6 thru 9 (190°C &
230°C) illustrate the effect of various concentrations of polyamide in
10   maleic anhydride grafted substantially linear ethylene elastomers on
these same rheological and elastic modulus properties. These figures
illustrate the new nylon modified Engage elastomers possess not only a
tremendous increase in shear sensitivity, but a significantly higher
melt elasticity (lower Tan Delta) than a typical Engage* polymer
15   (exemplary of a narrow dispersity ethylene polymer). It is
interesting to note that the slope of the viscosity curve at 190°C
(below the melting point of Nylon 6) shows little change from the
slope of the viscosity curve at 230°C (above the melting point of
Nylon 6) just the expected shift due to higher temperatures.
20

control samples failed at about 60°C, while ITP-g-MAH/PBT was stable
up to 120°C. The rheology comparison is shown in Figure 2. The
results show that the ITP-g_MAH/PBT is a thermoplastic elastomer with
improved processability and enhanced pseudo plastic ("shear

5   thinning") behavior. As set forth in Figure 19, the ITP-g-MAH/PBT
blend also has improved tensile properties compared to ITP alone. Tan
delta data taken from DMS testing in Figure 2 & 3 also indicates these
materials should be useful in blow molding and thermoforming
applications.

10

Example 2

        The composition was produced by mixing and melt blending ITP-g-
MAH (133g) and MMA/GMA acrylic copolymer (57 g) in a Haake System 90
torque rheometer at 230°C for 10 minutes. The resulting mixture was

15   subsequently cooled to ambient temperature and pelletized using a
mill. The RSA results in Figure 4 indicate the reactive blend of ITP-
g-MAH/(MMA/GMA) has high service temperature, i.e., the sample is
stable up to 110°C.

20 .   Although this invention has been described in considerable
detail through the preceding examples, such detail is for the purpose
of illustration only and is not to be construed as a limitation upon
the invention. Many variations can be made upon the preceding
examples without departing from the spirit and scope of the invention

25   as described in the following claims.

Examples 3-7

        The nylon (exemplary of an engineering thermoplastic) modified
elastomers explored during the course of this research are listed in

30   Table 1. These compositions were prepared by dry blending the maleic
anhydride grafted elastomers MAH modified Engage[+]8200 (Trademark of
The Dow Chemical Company) (EG 8200 MAH) with Nylon 6 at the specified
ratios and melt mixed at 260°C on a 35mm Werner-Pfleiderer co-
rotating, twin screw extruder at a speed of 250 rpm. Each extruded

35   modified elastomer was passed through a ice water bath, chopped into

89

The branched block ethylene polymer contained in the
compositions of Examples 8-24 is prepared by dry blending Nylon 6
(having a weight average molecular weight of 22,000 and a melt index
of 7), and an ethylene polymer containing a maleic anhydride branch

5   point ("E/MAH polymer") in amounts, respectively, as shown below. The
maleic anhydride branch point is formed on the E/MAH polymer, using a
peroxide initiator, in an amount of about 1 weight percent based on
the weight of the E/MAH polymer. The dry blend of nylon 6 and the
E/MAH polymer is then melt mixed in a 30 mm Werner & Pfleiderer

10   extruder to cause the nylon 6 to react with the maleic anhydride
branch point and add as the final block on the E/MAH copolymer to form
a branched block ethylene polymer. Conditions used in such reactive
extrusion are: zone temperatures of 150, 200, 250, 250 and 250°C; 250
rpm; 40-65 percent torque; and a 30 second residence time. The

15   branched block ethylene polymer is passed through an ice water bath,
chopped into granules and collected for blending with a thermoplastic
molding polymer.

The final compositions of Examples 8-24 and Controls A-I are

20   prepared by mixing the dry components of each on a paint shaker for 5
minutes, and then feeding the dry-blended formulation to the Werner &
Pfleiderer extruder under the same conditions used to prepare the
branched block ethylene polymer, except that the zone temperatures are
150, 200, 280, 280 and 280°C. The extrudate is again cooled in the

25   form of strands and comminuted as pellets. The pellets are dried in
an air draft oven for 3 hours at 120°C, and are then used to prepare
test specimens on a 70 ton Arburg molding machine on which the barrel
temperaturs are 200°C (feed), 250°C, 250°C and 255°C (nozzel), the
mold temperature is 80°F, and the screw speed is 120 rpm. Samples are

30   not annealed before testing.

The formulation content of Examples 8-13 and of Controls A-D is
given below in Table II, in parts by weight of the total composition.

35   In Table I:
          "Polypropylene" is Profax_ 6323 polypropylene from Himont having
          a melt index of about 12, one of the types of polyolefin resin
          described above as a blend component (b);

40   "HDPE" is high density polyethylene having a density of about

92

Table 1

Branched Block Ethylene Polymers wherein the Reactive Thermoplastic is
Nylon 6

Example:	3	4	5	6	7
Engage* 8200 /MAH	1800	1700	1600	1500	1400
Nylon 6	200	300	400	500	600
weight percent nylon	10	15	20	25	30

5

* Ethylene polymers commercially available from The Dow Chemical
Company

Polymers of the invention whose characteristics are represented
10   in Figures 4-18 are prepared as in Examples 3-7. The polymers of
Figures 1-2a, 2b are prepared as those of Examples 1 and 2.

The tan delta value of the branched block ethylene polymer of
this invention is also superior to that of either a homogeneous
15   ethylene polymer or a branched homogeneous ethylene polymer, and is
indicative of significantly high melt elasticity (high storage
modulus) at low as well as at high shear. Moreover, it is found that
the branched block ethylene polymer of this invention has the
corresponding effect on a blend of a molding polymer therewith. Such
20   a blended composition displays greater shear sensitivity and greater
melt elasticity at low shear than a composition modified with just a
homogeneous ethylene polymer or a branched homogeneous ethylene
polymer.

25   Examples 8-24: Use of Branched Block Ethylene Polymers wherein the
Reactive Thermoplastic Polymer of Subcomponent(c) is an Amine-
Functionalized Polymer:

91

Table II

Content of

Examples 8-13 and Controls A-D

| | Controls | | | | Examples | | | | | |
	A	B	C	D	8	9	10	11	12	13
Polypropylene	2,000	1,500	1,500	1,500	1,600	1,500	1,400	1,500	1,500	
HDPE										1,600
Ethylene Polymer		500		350						
E/MAH Copolymer			500					200		
Nylon 6				150						
Branched Block Ethylene Polymer I					400	500	600	300		400
Branched Block Ethylene Polymer II									500	
Percent Ethylene Polymer	0	25	24.8	17.5	14.0	17.5	21.0	20.4	17.3	19.0

94

0.96 g/cm3 and an I2 melt index (according to ASTM D 1238) of about 35, another of the types of polyolefin resin described above as a blend component (b);

5   "Ethylene Polymer" is a "substantially linear" ethylene polymer, having a density of about 0.87 g/cm^3, which does not contain a maleic anhydride branch point;

"E/MAH Copolymer" is a "substantially linear" ethylene polymer,
10   having a density of about 0.87 g/cm3, containing maleic anhydride as a branch point in an amount of about 1.0 wt%;

"Nylon 6" is Capron_ 8207 polyamide from Allied Signal, having a melt index of about 7, and a weight average molecular weight of
15   about 22,000;

"Branched block ethylene polymer I" is a branched block ethylene polymer prepared from (i) 70 weight percent E/MAH copolymer having an I2 of about 0.5, in which the ethylene polymer is a
20   "substantially linear"; and (ii) 30 weight percent nylon 6;

"Branched block ethylene polymer II" is a branched block ethylene polymer prepared from (i) 80 weight percent Tafmer_ P-0180, a linear, narrow MWD ethylene polymer from Mitsui
25   Petrochemical which contains polypropylene, and which has a density of 0.869 g/cm3, an I2 melt index of 4, and a maleic anhydride branch point; and (ii) 20 weight percent nylon 6; and

"Percent Ethylene Polymer" is the weight percent of ethylene
30   polymer present in the blended composition, whether the ethylene polymer does not contain a branch point, is in the form of an E/MAH copolymer, or has been formed into a branched block ethylene polymer.

D 790. Results are reported in kpsi.

The following tests of physical and mechanical properties are
performed on samples of the compositions of Examples 8-13 and Controls
A-D, and the results of these tests are shown in Table II:

5

Rheology Index involves the viscosity of a sample determined
from Rheometric Mechanical Spectroscopy, in which the sample is placed
between plates which rotate reciprocatingly in the plane of the
sample. The sample is heated to a specified temperature above its
10   softening point, and viscosity is determined by the power required to
force the plates to rotate at varying frequencies. Shown in Table II
is a unitless value obtained as a ratio of the viscosity of the sample
at 190°C when the plates are rotating at 0.1 radians/second divided by
the viscosity at 100 radians/second.

15

Impact resistance ("Izod") is measured by the Izod test
according to ASTM Designation D 256-84 (Method A) at 25°C. The notch
is 10 mils (0.254 mm) in radius. Izod results are reported in ft-
lb/in.
20   Impact resistance ("Weldline") is also measured by the Izod test
according to ASTM Designation D 256-84 (Method A) at 25°C, but with
respect to a sample which is formed with a butt weld in a double gated
mold. The sample is unnotched, and it is placed in the vise so that
the weld is 1 mm above the top surface of the vise jaws. Weldline
25   results are also reported in ft-lb/in, except as to Example 5 where
"N.B." indicates that the sample did not break.

The dart drop impact test ("Dart Drop") is performed at 23°C by
dropping a 100 pound weight which carries a ½" dart onto a circular
30   test sample which is 1/8" thick. The weighted dart falls freely on a
slotted track at 8050 in/min and impacts the sample, which is secured
in position in the path of descent on an aluminum cast base. The
value recorded in Table II is the energy required for the dart to
break the sample, expressed in in-lb.
35   Deflection temperature under load ("D.T.U.L.") is measured in
accordance with ASTM Designation D 648-82 at 66 psi. Results are
reported in °F.

Flexural modulus ("F. Modulus") is determined according to ASTM

The data in Table III demonstrate that a branched block ethylene polymer is effective, when combined with a molding polymer such as a polyolefin resin, in producing a composition with a desirable balance

5   of properties. A higher Rheology Index value is particularly notable because a higher value indicates greater shear sensitivity. A large numerator in this ratio shows that a material holds its melt strength at low shear, and a small denominator shows that a material undergoes shear thinning for easier processing, both of which typically are

10   desirable qualities. The balance of properties shown for the examples is attained despite the fact that each of them contains less ethylene polymer than either Controls A or B. From the data in Table III, it can be concluded that a very effective means of utilizing an ethylene polymer in a blend composition is to use it to prepare a branched

15   block ethylene polymer (as described herein), and then employ the branched block ethylene polymer as a modifier with a molding polymer. Compared to Controls A and B, the examples had greater surface durability and resistance to scratching.

20   The compositions of Examples 14-18 and Control E are prepared in the same manner as the compositions of Examples 8-13 and Controls A-D. The formulation content of Examples 14-18 and of Control E is given below in Table IV, in parts by weight of the total composition. In Table IV, "Polypropylene", "E/MAH Copolymer" and "Branched Block

25   Ethylene Polymer I" are the same as in Table II. Branched block ethylene polymers prepared from smaller amounts of polyamide than branched block ethylene polymer I are used in the compositions of Examples 14-17, however, and these are designated in Table IV as follows:

30

"Branched Block Ethylene Polymer III" is a branched block ethylene polymer prepared from 90 weight percent "substantially linear" ethylene polymer, having an I2 melt index of about 0.5 and containing a maleic anhydride branch point; and 10 weight

35   percent nylon 6;

"Branched Block Ethylene Polymer IV" is a branched block ethylene polymer prepared from 85 weight percent "substantially linear" ethylene polymer, having an I2 melt index of about 0.5

98

Table III

Properties of

Examples 8-13 and Controls A-D

| | Controls | | | | Examples | | | | | |
	A	B	C	D	8	9	10	11	12	13
Rheology Index	4.9	4.7	5.9		10.4	18.2	25.4		16.5	
Izod, ft-lb/in	0.4	2.0	2.8	1.6	2.4	12.1	15.2	3.2	5.7	10.6
Weldline, ft-lb/in	7.6	8.0	4.5	2.5	17.3	16.8	22.4	11.8	4	N.B.
Dart Drop, In-lb	65	304	282	230	344	341	314	312	279	237
D.T.U.L., °F	170	140	138	149	142	140	134			
F. Modulus, kpsi	159	112	120	155	114	113	104			

97

Table IV

Content of Examples 14-18 and Control E

	Control	Examples				
	E	14	15	16	17	18
Polypropylene	1,500	1,500	1,500	1,500	1,500	1,500
E/MAH Copolymer	500					
Branched Block Ethylene Polymer I						500
Branched Block Ethylene Polymer III		500				
Branched Block Ethylene Polymer IV			500			
Branched Block Ethylene Polymer V				500		
Branched Block Ethylene Polymer VI					500	
Percent nylon in the Branched Block Ethylene Polymer	0	10	15	20	25	30
Percent nylon, composition	0	2.5	3.75	5.0	6.25	7.5

and containing a maleic anhydride branch point; and 15 weight
percent nylon 6;

5   "Branched Block Ethylene Polymer V" is a branched block
ethylene polymer prepared from 80 weight percent "substantially
linear" ethylene polymer, having an I2 melt index of about 0.5
and containing a maleic anhydride branch point; and 20 weight
percent nylon 6; and

10   "Branched Block Ethylene Polymer VI" is a branched block
ethylene polymer prepared from 75 weight percent "substantially
linear" ethylene polymer, having an I2 melt index of about 0.5
and containing a maleic anhydride branch point; and 25 weight
percent nylon 6.

15

Percent nylon by weight is also set forth in Table III for each
of the branched block ethylene polymer and for each composition as a
whole.

20   The same tests for physical and mechanical properties are
performed on Examples 14-18 and Control E as are performed on Examples
7-13 and Controls A-D, except that melt strength for each branched
block ethylene polymer is determined using a pulley/drum type melt
tension tester, as described above, and is measured in centiNewtons.
25   The results of such tests are set forth in Table V.

Table V

Properties of

Examples 14-18 and Control E

	Control	Examples				
	E	14	15	16	17	18
Izod, ft-lb/in	2.8	2.5	3.2	8.3	9.7	12.1
Weldline, ft-lb/in	4.5	5.4	6.8	9.4	9.9	16.8
Dart Drop, in-lb	282	310	310	306	305	341
Rheology Index	5.9	11.5	11.4	12.7	14.1	18.2
D.T.U.L., °F	138	144	138	141	144	140
F. Modulus, kpsi	120	105	127	122	124	113
Branched block ethylene polymer melt strength, cN	13.8	22.9	25.9	32.2	45.4	52.2

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Table VI, Content and Properties
of Examples 19-20 and Controls F-G

	Control F	Example 19	Control G	Example 20
Polypropylene	1,500	1,500	1,500	1,500
E/MAH Copolymer	350		350	
Nylon 6	150		150	
Branched Block Ethylene Polymer VI		500		500
Percent nylon, composition	7.5	7.5	7.5	7.5
Izod, ft-lb/in	1.6	12.1	2.0	12.7
Weldline, ft-lb/in	10.9	16.8	5.7	13.3
Dart drop, in-lb	320	341	288	314
D.T.U.L., °F	143	140	139	143
F. Modulus, kpsi	112	113	115	117
Method of mixing	extrusion	extrusion	Banbury	Banbury

The results of Examples 14-18 and Control E are further
evidence of the balance of desirable properties obtainable from the
used of a branched block ethylene polymer as a modifier in a blended
5   composition. It can be seen that, within the ranges in which
polyamide is used in this invention to form the final block of the
branched block ethylene polymer, increasing the amount of polyamide
used increases the Izod properties.

10   The compositions of Example 19 and Control F are prepared in
the same manner as the compositions of Examples 8-18 and Controls A-
E. The compositions of Example 20 and Control G (although containing
materials from which a branched block ethylene polymer could have
been, but was not, made) are prepared by mixing the components
15   simultaneously in a Banbury mixer at 220°C for 12 minutes. The
formulation content of Examples 19-20 and of Controls F-G is given
below in Table V, in parts by weight of the total composition. In
Table V, "Polypropylene", "E/MAH Copolymer" and "Branched block
ethylene polymer VI" are the same as in Table III. "Nylon 6" is the
20   same as in Table II. Percent nylon by weight is also set forth in
Table VI for each composition as a whole.

Some of the same tests for physical and mechanical properties
are performed on Examples 19-20 and Controls F-G as are performed on
25   Examples 8-18 and Controls A-E, and results of such tests are also
set forth in Table VI.

notably higher viscosity at a low shear rate than either an ethylene
polymer or a branched ethylene polymer, and yet also shows a notably
higher shear sensitivity than either of its precursors since its
viscosity at high shear drops to about the same level as that

5   displayed by an ethylene polymer or a branched ethylene polymer. The
tan delta value of a branched block ethylene polymer is also superior
to that of either an ethylene polymer or and a branched ethylene
polymer, and is indicative of significantly high melt elasticity (high
storage modulus) at low as well as at high shear.

10

       Moreover, it is found that a branched block ethylene polymer has
the corresponding effect on a blend of a molding polymer therewith.
Such a blended composition displays greater melt strength and
elasticity at low shear than a composition modified with just an

15   ethylene polymer or a branched ethylene polymer, and yet such a blend
is shear sensitive enough that it thins at high shear to essentially
the same viscosity as does a branched ethylene polymer. For example,
Figure 20 shows viscosity at various shear rates for polypropylene
blended with an ethylene/branch point copolymer, and with a branched

20   block ethylene polymer prepared from various levels of polyamide as
the amine-functionalized copolymer. The blends containing a branched
block ethylene polymer have a higher viscosity at low shear but thin
at high shear to the same extent as the blend containing only an
ethylene/branch point copolymer. Figure 21 shows, for the same group

25   of blends, tan delta, which is lost modulus divided by storage
modulus. The compositions in which polypropylene is blended with a
branched block ethylene polymer, instead of just an ethylene/branch
point copolymer, have a lower tan delta and thus a higher storage
modulus. Higher storage modulus represents a greater amount of

30   recoverable elasticity. The determination of tan delta values is
based on known methods, such as those derived from Melt Rheology and
Its Role in Plastics Processing, Dealy and Wissbrun, Van Nostrand,
1990.

35   These improvements in properties are believed to be related to a
tendency of the branched block ethylene polymer to be dispersed in a
blended composition in such manner that the amine-functionalized
polymer is dispersed as sub-micron particles, having great uniformity
of size, within particles of the branched ethylene polymer. By

40   contrast, when an amine-functionalized polymer is simply mixed as a

The results of Examples 19-20 and Controls F-G demonstrate the
importance, when blending branched ethylene polymer and an amine-
5   functionalized polymer (such as a polyamide) with a molding polymer
(such as a polyolefin resin), of performing the mixing under
conditions such that a branched block ethylene polymer is formed from
the branched ethylene polymer and the amine-functionalized polymer.
Such conditions include either first preparing the branched block
10   ethylene polymer in a separate apparatus and then blending it with the
molding polymer, or mixing all three materials in the same apparatus,
such as an extruder, but in a sequence which allows the amine-
functionalized polymer to react with the branched ethylene polymer, to
form the branched block ethylene polymer, before the presence of the
15   molding polymer would hinder that reaction.

For instance, the composition of Control F is a blend with
polypropylene of the components from which a branched block ethylene
polymer could have been made. However, the preparation of Control F
20   did not produce a branched block ethylene polymer in a blend with
polypropylene because all three components of Control F are dry
blended together and then melt mixed simultaneously in an extruder.
When the same components are used in Example 19 to first prepare a
branched block ethylene polymer, from an E/MAH branched ethylene
25   polymer and a polyamide, the resulting blend with polypropylene
produces a composition which shows notably higher Izod, Weldline and
Dart drop values. Even when the simultaneous blending of the E/MAH
branched ethylene opolymer, polyamide and a polyolefin resin occurs
under the high temperture, high shear conditions of a Banbury mixer,
30   as in Control G, the resulting properties of the blended composition
are no better than those of Control F, and are notably inferior to
those of Example 20, in which preparation of a branched block ethylene
polymer is completed before melt mixing with a molding polymer is
undertaken.
35

It is found, in general, that a branched block ethylene polymer
exhibits improved rheological properties as compared to the components
from which it is made. For example, a branched block ethylene
polymer, when tested by dynamic mechanical spectroscopy, shows a

of forming a branched block ethylene polymer can be lost if an
excessive amount of amine-functionalized polymer is used. The value
added by the amine-functionalized polymer, which forms the final block
on the branched block ethylene polymer, will be offset by free amine-
5   functionalized polymer, which may crosslink or may form crystalline
domains which are brittle and subject the blended composition to
increased notch sensitivity.

The compositions of Examples 21-24 and Controls H and I are
10   prepared using similar mixing conditions as the compositions of
Examples 8-18 and Controls A-E. However, Controls H and I are
representative of a situation in which a branched block ethylene
polymer could have been prepared, but was not, since all components
were mixed together rather than in a sequence which would allow
15   formation of a branched block ethylene polymer. The formulation
content of Examples 21-24 and Controls H and I is given below in Table
VII, in parts by weight of the total composition. In Table VII:

"Polycarbonate" is 10 melt flow Bisphenol-A polycarbonate;
20

" Branched Block Ethylene Polymer VII" is a branched block
ethylene polymer prepared from 70 weight percent E/MAH copolymer
having an I2 melt index of 0.37; and 30 weight percent nylon 6;

25   "Epoxy" is a Bisphenol-A/epichlorohydrin epoxy resin, such
as D.E.R._ 332 epoxy resin from The Dow Chemical Company;

E.S.O. is epoxidized soybean oil tackifier; and

30   IR 1076 is Irganox_ 1076 stabilizer.

Also in Table VI, "Nylon 6", "Branched Block Ethylene Polymer I"
and "E/MAH Copolymer" are the same as in Table II. Percent E/MAH
Copolymer by weight is also set forth in Table VII for Controls H and
35   I and Examples 16-17 as a whole.

Some of the same tests for physical and mechanical properties
are performed on Examples 14-17 and Controls H and I as are performed
on Examples 1-11 and Controls A-E. Other tests performed are as

component in a random, physical blend with an branched ethylene
polymer without first being formed into a branched block ethylene
polymer, the amine-functionalized polymer which is dispersed within
the ethylene polymer has little or no uniformity of particle size; and

5   the amine-functionalized polymer may also in such case be dispersed as
large, multi-micron particles in the molding polymer matrix resin with
no association to the ethylene polymer whatever.

Consequently, in a preferred embodiment, the amine-
10   functionalized polymer in a branched block ethylene polymer is
dispersed in an branched ethylene polymer as particles about 50% or
more, often about 65% or more, frequently about 80% or more and
occasionally about 90% or more of which have a size which is within
about 80% to about 120% of the average size of the whole population of

15   amine-functionalized polymer particles dispersed in the particle of
branched ethylene polymer.

When an amine-functionalized polymer in a branched block
ethylene polymer is dispersed in the branched ethylene polymer as a
20   population of particles which are very uniformly of small size, the
particles of branched ethylene polymer are themselves smaller and are
more evenly distributed within the molding polymer matrix, which
results in a composition which has superior elastomeric impact
strength. By contrast, when an amine-functionalized polymer particle

25   is merely a component in a random, physical blend with no branched
block ethylene polymer terpolymer, branched ethylene polymer particles
are larger and/or groups of branched ethylene polymer particles tend
to agglomerate and create domains which effectively behave as if they
were larger particles. Therefore, in another preferred embodiment,

30   the ratio of the size of an branched ethylene polymer particle to the
average size of an amine-functionalized polymer particle dispersed
therein, when a branched block ethylene polymer has been prepared
therefrom, is much lower than the ratio of the size of an branched
ethylene polymer particle to the average size of an amine-

35   functionalized polymer particle dispersed therein when a branched
block ethylene polymer has not been formed and the amine-
functionalized polymer is merely a component in a random, physical
blend.

40   Corrrespondingly, the beneficial effect in a blended composition

107

Table VII, Content of Examples 21-24 and Controls H-I

	Example 21	Example 22	Control H	Example 23	Control I	Example 24
Polycarbonate	1850	1850				
Nylon 6			1700	1570	1600	1428
Branched Block Ethylene Polymer I				430		572
Branched Block Ethylene Polymer VII	150	150				
E/MAH Copolymer			300		400	
Epoxy		4				
E.S.O.	2	2				
IR 1076	4	4				
Percent E/MAH Copolymer in composition			15	15	20	20

follows:

Tensile strength at break and percent elongation at break are both measured in accordance with ASTM Designation D 638-84.

5

Gloss measurements are performed on testing samples according to ASTM Designation D 523-85 using a Dr. Lange Reflectometer RB3 available from Hunter Assocaiates.

10   The results of each of these tests are set forth in Table VII.   N.B. indicates no break in the weldline test.

The results of Controls H and I and Examples 23 and 24 demonstrate that an Ethylene/MAH Copolymer, when used by itself as an impact modifier without having been formed into a branched block

5   ethylene polymer, does not enhance impact properties to the same extent that a branched block ethylene polymer does. An Ethylene/MAH Copolymer has a lower viscosity and a lower elasticity than a branched block ethylene polymer. Consequently, when an amine-functionalized polymer is utilized as just another blend component rather than being

10   utilized to prepare a branched block ethylene polymer, the resulting composition is not characteried by impact proerties, particularly at low temperature, which are as desirable as a composition of a block.

Examples using branched block ethylene polymers in which the reactive
15   thermoplastic polymer of subcomponent (c) is a polyester.

The composition of Example 25 is a blend with polycarbonate of a branched block ethylene polymer. The composition of Control A1 is a blend with polycarbonate of the three components from which a branched

20   block ethylene polymer could have been made. However, the preparation of Control A did not result in a blend with polycarbonate of a branched block ethylene polymer because all four materials were blended simultaneously. The composition of Control B1 is a blend with polycarbonate of an ethylene polymer containing only a maleic

25   anhydride branch point ("E/MAH copolymer"). The composition of Controls C1 and D1 is each a blend with polycarbonate of a substantially linear ethylene polymer which does not contain a branch point. The compositions of Controls E1, F1, and G1 is each a blend with polycarbonate of another type of olefin polymer.

30

The branched block ethylene polymer contained in the composition of Example 25 is prepared by melt blending in a 30 mm Werner & Pfleiderer extruder a mixture of 30 weight percent poly(butylene terephthalate) and 70 weight percent "substantially linear" ethylene

35   polymer containing a maleic anhydride branch point ("E/MAH Copolymer"). The maleic anhydride branch point is formed on the "substantially linear" ethylene polymer in an amount of 1 weight

112

Table VIII, Properties of Examples 21-24 and Controls H-I

	Example 21	Example 22	Control H	Example 23	Control I	Example 24
Izod, ft-lb in, 23°C	13.7	13.7	6.7	8.2	5.6	7.5
Izod, ft-lb in, 0°C	12.8	13.1	6.6	9.0	6.9	8.9
Izod, ft-lb in, -20°C	11.7	10.6	2.4	2.8	3.6	9.0
Izod, ft-lb in, -30°C						9.6
Weldline, ft-lb/in	3.0	7.0	N.B.	N.B.	N.B.	N.B.
20° Gloss	18	19				
60° Gloss	69	70				
Tensile Strength	8030	8791	5828	5602	7001	6619
Percent Elongation	84	111	41	60	181	189
D.T.U.L., °F	291	288	289	335	299	307
F. Modulus, kpsi	290	299	205	198		228

"POE" is a "substantially linear" ethylene polymer which does not
contain a maleic anhydride branch point, having a 0.5 I2 melt index;

"ECO" is ethylene/carbon monoxide copolymer;

5

"HDPE" is high density polyethylene having a density of about 0.96
g/cm3 and an I2 melt index (according to ASTM D 1238) of about 10; and

"LLDPE" is a linear low density polyethylene having an I2 melt index
10   (according to ASTM D 1238) of about 4.

The following tests are performed on Example 25 and Controls A1-G1,
and the results of these test are also shown in Table I:

15   Impact resistance is measured by the Izod test ("Izod") according to
ASTM Designation D 256-84 (Method A) at 25°C. The notch is 10 mils
(0.254 mm) in radius. Impact is parallel to the flow lines in the
plaque from which the bar is cut in one sample of each composition and
is perpendicular to flow lines in another sample. The ratio of the
20   Izod result in the case of impact parallel to flow lines to that of
impact perpendicular to flow lines is set forth as a unitless value
labled "Anisotropy". The Izod results are then used to estimate the
ductile/brittle transition temperature ("DBTT") of each sample.
Impact resistance is also measured by the Izod test ("Weldline")
25   according to ASTM Designation D 256-84 (Method A) at 25°C, but with
respect to a sample which is formed with a butt weld in a double gated
mold. The sample is unnotched, and it is placed in the vise so that
the weld is 1 mm above the top surface of the vise jaws. Weldline
results are reported in kg-cm/cm.
30

percent, based on the weight of the E/MAH Copolymer, using a peroxide initiator. The conditions used in preparation of the branched block ethylene polymer are: zone temperatures of 150, 200, 250, 250 and 250°C; 250 rpm; 70-85 percent torque; and a 30 second residence

5 time.

The final compositions of Example 25 and Controls A1-G1 are prepared by mixing the dry components of each on a paint shaker for 5 minutes, and then feeding the dry-blended formulation to the Werner &

10 Pfleiderer extruder under the same conditions used to prepare the branched block ethylene polymer, except that the zone temperatures are 150, 200, 280, 280 and 280°C. The extrudate is cooled in the form of strands and is then comminuted as pellets. The pellets are dried in an air draft oven for 3 hours at 120°C, and are then used to prepare

15 test specimens on a 70 ton Arburg molding machine on which the barrel temperature is 280°C, the mold temperature is 82°C, and the screw speed is 120 rpm.

The formulation content of Example 25 and of Controls A1-G1 is

20 given below in Table I, in parts by weight of the total composition. In Table I:

"Polycarbonate" is a Bisphenol-A polycarbonate having a weight average molecular weight of approximately 28,000;

25

"Branched block ethylene polymer" is a branched block ethylene polymer prepared from poly(butylene terephthalate) and a "substantially linear" ethylene polymer containing a maleic anhydride branch point, as described above;

30

"E/MAH Copolymer" is a substantially linear ethylene polymer containing a maleic anhydride branch and having a 0.5 I2 melt index;

"PBT" is poly(butylene terephthalate);

35

113

The data in Table IX demonstrate that a branched block ethylene polymer is effective, when combined with a molding polymer, in producing a composition with a desirable balance of properties.

5   Control A1, which contains the components from which a branched block ethylene polymer in a PC blend could have been made but was not, has a weldline value much lower than that of Example 25. The other controls, which each contain some other form of olefin polymer, have properties which are, in individual categories, quite good, but none

10   of them has as desirable a balance in all three catagories as Example 25. For instance, Controls C1-E1 all have an impressive level of anisotropy but suffer from very low weldline. From the data in Table VIII, it can be concluded that a very effective means of utilizing an olefin polymer in a blend composition is to use it to prepare a

15   branched block ethylene polymer (as described herein), and then employ the branched block ethylene polymer as a blending modifier with a molding polymer.

These improvements in properties are believed to be related to a tendency of the branched block ethylene polymer to be dispersed in a

20   blended composition in such manner that the polyester is dispersed as sub-micron particles, having great uniformity of size, within particles of the ethylene/branch point copolymer. By contrast, when a polyester is simply mixed as a component in a random, physical blend with an ethylene/branch point copolymer without first being formed

25   into a branched block ethylene polymer, the polyester which is dispersed within the ethylene polymer has little or no uniformity of particle size; and the polyester may also in such case be dispersed as large, multi-micron particles in the molding polymer matrix resin with no association to the ethylene polymer whatever.

30

Table IX, Content and Properties

of Controls A1-G1 and Example 25

| | Controls | | | | | | | Example 25 |
	A1	B1	C1	D1	E1	F1	G1	
Polycarbonate	93	95	93	95	95	95	95	93
Branched block ethylene polymer								7
E/MAH Copolymer	4.9	5						
PBT	2.1		2.1					
POE			4.9	5				
ECO					5			
HDPE						5		
LLDPE							5	
Anisotropy	.678	.748	.853	.879	.838	.575	.672	.783
DBTT, °C	-35	-45	-20	-20	-20	-40	-30	-35
Weldline, kg-cm/cm	32	26	17	5	7	29	12	83

in a random, physical blend with no terpolymer formation, ethylene/branch point copolymer particles are larger and/or groups of ethylene/branch point copolymer particles tend to agglomerate and create domains which effectively behave as if they were larger

5   particles. Therefore, in another preferred embodiment, the ratio of the size of an ethylene/branch point copolymer particle to the average size of a polyester particle dispersed therein, when a branched block ethylene polymer has been prepared therefrom, is much lower than the ratio of the size of an ethylene/branch point copolymer particle to

10   the average size of a polyester particle dispersed therein when a block copolymer has not been formed and the polyester is merely a component in a random, physical blend.

The compositions of Examples 26-29 are prepared in a similar manner as the composition of Example 25. The branched block ethylene

15   polymer used in the compositions of Examples 26-28 was prepared by reacting poly(ethylene terephthalate), having an intrinsic viscosity of 0.59, and a "substantially linear" ethylene polymer containing a maleic anhydride branch point in the presence of potassium paratolyl sulfimide ("KPTSM") catalyst. Although the branched block ethylene

20   polymer prepared with the benefit of catalyst is more preferred, that which is prepared without catalyst, such as used in Example 26, is still a useful product. The branched block ethylene polymer used in each example is prepared from 30 weight percent "substantially linear" ethylene polymer containing a maleic anhydride branch point and 70

25   weight percent poly(ethylene terephthalate). Each blended composition is prepared from 93 weight percent polycarbonate and 7 weight percent branched block ethylene polymer. The amount of KPTSM catalyst used in Examples 27-29, expressed in weight parts per million measured with respect to the combined weight of the E/MAH Copolymer and the

30   poly(ethylene terephthalate) from which the branched block ethylene polymer is made, is shown in the following table.

The impact resistance of Examples 26-29 is measured by the Izod test according to ASTM Designation D 256-84 (Method A) at 25°C with respect to a "weldline" sample which is formed with a butt weld in a

35   double gated mold. The sample is unnotched, and it is placed in the vise so that the weld is 1 mm above the top surface of the vise jaws. Izod results for Examples 26-29 are reported for 11 trials of the composition of each example, and the results of each of those 11

Consequently, in a preferred embodiment, the polyester in a
branched block ethylene polymer is dispersed in an ethylene/branch
point copolymer as particles about 50% or more, often about 65% or
more, frequently about 80% or more and occasionally about 90% or more

5   of which have a size which is within about 80% to about 120% of the
average size of the whole population of polyester particles dispersed
in the particle of ethylene/branch point copolymer.

When a polyester in a branched block ethylene polymer is
dispersed in the ethylene/branch point copolymer as a population of

10 particles which are very uniformly of small size, the particles of
ethylene/branch point copolymer are themselves smaller and are more
evenly distributed within the molding polymer matrix, which results in
a composition which has superior elastomeric impact strength. By
contrast, when a polyester particle is merely a component

	Examples			
	26	27	28	29
Amount of KPTSM, ppm	0	500	1,000	2,000
Samples out of 11 with no break	3	7	7	7
Samples out of 11 with partial break	5	2	4	4
Samples ot of 11 with brittle break	3	2	0	0
Unnotched Izod, ft-lb/in	20	20	34	43
Standard deviation - Izod, ft-lb/in	13	15	2	1

5   The results of Examples 26-29 demonstrate that the presence of
KPTSM as a catalyst, during the preparation of the branched block
ethylene polymer used as a blending modifier in the compositions of
Examples 27-29, produced a branched block ethylene polymer which made
a better contribution to the impact strength of the composition than
did the branched block ethylene polymer prepared without benefit of a
10   catalyst. While the composition of Example 26 showed a very
respectable Izod value, the compositions of Examples 27-29 showed
improved Izod and fewer brittle breaks as greater amounts of the KPTSM
catalyst were used during preparation of the branched block ethylene
polymer used in the blend.

15

Example 30: Use of Branched Block Ethylene Polymers Wherein the
Reactive Thermoplastic Polymer is Polycaprylactone

Bisphenol A polycarbonate with a weight average molecular weight of
20   18,000 grams/mole was used as the base resin. The polyolefin phase
used was a substantially linear ethylene/1-octene polymer having a
density of 0.88 g/cc and an I2 of 30 g/10 min. The
ethylene/propylene/non-conjugated diene elastomer grafted with
styrene/acrylonitrile was obtained from Uniroyal Chemical under the
25   tradename Royaltuff 372P20 (SAN-g-EPDM). The poly(caprolactone) (PCL)
was obtained from Union Carbide under the tradename Tone P-767.

trials are clasified as either "no break", "partial break" or "brittle break". A brittle break of a sample in the following table refers to a break which resulted in separation of the sample into two disctinct pieces, whereas in a partial break, the sample is not cleanly
5 separated and the major portions remain hinged. The numerical Izod value reported for each example is the average of that value for those of the 11 trials of each which were partial or brittle breaks. Izod results are reported in ft-lb/in, as is the standard deviation of the Izod values for each group of partial or brittle breaks.

Performance attributes

5

	Molded PC (Mw) g/mol	Nu at 80 sec^{-1}	Nu at 2900 sec^{-1}	DBTT	Room temp. IZOD
Control 1	18500	191	108	greater than 30	2.2
Control 2	18500	152	70	-5	0
Example 1	18700	174	84	-20	8.8
Control 3	19200		100	-20	8.3
Example 2	18800	180	75	-10	9.1
Example 3	18600	163	72		8.8

A 70/30 weight ratio of MAH-g-EO was dry blended with PCL in a
tumbler. The mixture was pelletized using a 30 mm Werner & Pfleiderer
co-rotating twin-screw extruder. Extrusion conditions were screw
5 speed set at 245 rpm and barrel tempeatures set at 190, 260, 160,
260°C and die temperature set at 260°C. The following are the resin
compositions:

Resin Compositions
10

	Polycarbonate (80 MFR)	Homogeneous Ethylene Polymer (0.88 g/cc, 30 g/10 min.)	PCL-g-EO	SAN-g-EPDM
Control 1	100			
Control 2	90	10		
Example 1	90		10	
Control 3	90			10
Example 2	90	9	1	
Example 3	90	9		1

Molecular weight analysis: size exclusion chromatograph technique
couples with a UV detector using methylene chloride as the solvent and
tetrahydrofuran as the solvent carrier. Calibration was done with
15 LEXAN polycarbonate standard.

Viscosity (Nu): shear viscosity was determined using a capillary
rheometer and circular die with dimension of 1.27 mm inner diameter
and 25.4 mm length. The temperature used was 270°C. The reported
20 values were viscosity at 80 and 2900 sec^{-1}.

Izod Impact: Izod impact values were determined on a 0.25 mm (10
mils) prenotched sample. Tests were run using a 10 ft-lb pendulum.

25 Ductile brittle transition temperature (DBTT): the temperature at
which the sample has izod impact fracture going from ductile to
brittle.

7. The branched block ethylene polymer of Claim 1 wherein the narrow polydispersity ethylene polymer is a substantially linear ethylene polymer which is characterized as having

(i) a melt flow ratio I_{10}/I_2 which is greater than or
5 equal to 5.63, a

(ii) a molecular weight distribution defined by M_w/M_n which is less than or equal to $(I_{10}/I_2)-4.63$, and

(iii) a critical shear rate at the onset of surface melt fracture at least about 50 percent greater than a linear ethylene
10 polymer having essentially the same I_2 and M_w/M_n., each within 90-110 percent of the corresponding value for the substantially linear ethylene polymer; and

(iv) a single melting point as determined by diffrential scanning calorimetry between about 30 ° C and 150° C
15   wherein the substantially linear ethylene polymer is further characterized as having a SCBD Index of greater than 50 percent.

8. The branched block ethylene polymer of Claim 7 wherein the substantially linear ethylene polymer has a critical shear stress at
20 the onset of gross melt fracture greater than about 4 x 10^6 dyne/cm^2.

9. The branched block ethylene polymer of Claim 7 wherein the substantially linear ethylene polymer has an average of about 0.01 to about 3 long chain branches/1000 total carbon atoms.
25

10. The branched block ethylene polymer of Claim 8 wherein the substantially linear ethylene polymer has a processing index less than or equal to about 70 percent of the processing index of a linear ethylene polymer as to which the I_2, polydispersity and density is
30 each within 90-110 percent of the corresponding value for the substantially linear ethylene polymer.

11. The branched block ethylene polymer of Claim 1, wherein the reactive thermoplastic polymer is an amine-functionalized polymer.
35

-124-

What is claimed is:

1.   A branched block ethylene polymer comprising
        (a) an ethylene polymer;
5   (b) an ethylenically unsaturated functionalized organic
            compound; and
        (c) a reactive thermoplastic polymer capable of reacting with
            the ethylenically unsaturated functionalized organic
            compound.
10

2.   The branched block ethylene polymer of Claim 1 wherein the
ethylenically unsaturated functionalized organic compound contains a
carbonyl group.

15 3.   The branched block ethylene polymer of Claim 1 wherein the
ethylenically unsaturated functionalized organic compound is maleic
anhydride.

4.   The branched block ethylene polymer of Claim 1 wherein the
20 ethylenically unsaturated functionalized organic compound carries an
epoxy ring.

5.   The branched block ethylene polymer of Claim 1 wherein the
ethylenically unsaturated functionalized organic compound is an
25 oxazoline, amine or alcohol.

6.   The branched block ethylene polymer of claim 1, wherein the
ethylene polymer is a homogeneous ethylene polymer having:
        (i) a Mw/Mn ratio, as determined by gel permeation
30   chromatography, of less than about 3.0;
        (ii) a density of about 0.93 g/cm^3 or less; and
        (iii) a Short Chain Branching Distribution Index of greater than
            about thirty percent; and
        (iv)   a single melting peak as determined by differential
35   scanning calorimetry between -30°C and 150°C.

-123-

17.   The method of Claim 15 wherein the reactive thermoplastic
polymer is reacted with the branched ethylene polymer in the presence
of a catalyst selected from an alkali metal or alkaline earth metal
5   salt having a pKa of 7 or more, and a nitrogen-containing organic
base.

18.   The method of Claim 15 wherein the catalyst is an amine.

10   19.   The method of Claim 15 wherein the catalyst is derived from
an aromatic sulfimide.

20.   The method of Claim 15 wherein the catalyst is potassium
paratolyl sulfimide.

15

21.   The method of Claim 15 wherein both the formation of the
ethylenically unsaturated organic compound branch off of the ethylene
polymer, and (2) the reaction of the reactive thermoplastic polymer
with the ethylene polymer are performed in a single pass through one
20   extruder.

22.   A blend of a thermoplastic blending or molding polymer
with a branched block ethylene polymer which in turn comprises
     (a) an ethylene polymer;
25   (b) an ethylenically unsaturated functionalized organic compound;
and
     (c) a reactive thermoplastic polymer capable of reacting with the
ethylenically unsaturated functionalized organic compound.

30   23.   The blend of Claim 22, wherein the ethylene polymer is a
homogeneous ethylene polymer which has:
          (i) a Mw/Mn ratio, as determined by gel permeation
chromatography, of less than about 3.0;
          (ii) a density of about 0.93 g/cm^3 or less;
35   (iii) a Short Chain Branching Distribution Index of
greater than about thirty percent; and

-126-

13.   The branched block ethylene polymer of Claim 1, wherein the reactive thermoplastic polymer is a polyester.

14.   A method of preparing a branched block ethylene polymer which contains

(a) an ethylene polymer;

(b) an ethylenically unsaturated functionalized organic compound; and

(c) a reactive thermoplastic polymer capable of reacting with the ethylenically unsaturated functionalized organic compound;

said method comprising (1) forming the ethylenically unsaturated functionalized organic compound into a branch off of the ethylene polymer to form a branched ethylene polymer, and thereafter (2) reacting the reactive thermoplastic polymer with the branched ethylene polymer.

15.   The method of Claim 14, wherein the ethylene polymer is a homogeneous ethylene polymer having:

(i) a M_w/M_n ratio, as determined by gel permeation chromatography, of less than about 3.0;

(ii) a density of about 0.93 g/cm^3 or less;

(iii) a Short Chain Branching Distribution Index of greater than about thirty percent; and

(iv)   a single melting peak as determined by differential scanning calorimetry between -30°C and 150°C.

16.   The method of Claim 15, wherein the ethylene polymer is a substantially linear ethylene polymer which is characterized as having

(i) a melt flow ratio I_{10}/I_2 which is greater than or equal to 5.63, a

(ii) a molecular weight distribution defined by M_w/M_n which is less than or equal to $(I_{10}/I_2)-4.63$, and

(iii) a critical shear rate at the onset of surface melt fracture at least about 50 percent greater than a linear ethylene polymer having essentially the same I_2 and M_w/M_n, and

(iv) . a SCBD Index of greater than 50 percent.

-125-

(iv) a single melting peak as determined by differential scanning calorimetry between -30°C and 150°C.

24.   The blend of Claim 22, wherein the ethylene polymer is a
5   substantially linear ethylene polymer which is characterized as having
        (i) a melt flow ratio I_{10}/I_2 which is greater than or equal to 5.63, a
        (ii) a molecular weight distribution defined by M_w/M_n which is less than or equal to $(I_{10}/I_2)-4.63$, and
10   (iii) a critical shear rate at the onset of surface melt fracture at least about 50 percent greater than a linear ethylene polymer having essentially the same I_2 and M_w/M_n, and
        (iv) a SCBD Index of greater than 50 percent.

25.   The blend of Claim 22 wherein the thermoplastic blending or
15   molding polymer is selected from the group consisting of polycarbonate, polyester, poly(phenylene ether), polysulfone, polyetherimide, polypropylene, and polyethylene.

26.   The blend of Claim 22 wherein the thermoplastic blending or
20   molding polymer is a substantially linear ethylene polymer.

27.   The blend of Claim 22, further comprising a styrenic copolymer, an elastomeric impact modifier, a flow aid, or a mixture thereof.

25   28.   The blend of Claim 22, further comprising at least one of an oil or a filler.

29.   The blend of Claim 22, wherein the reactive thermoplastic polymer is nylon 6.
30.

30.   The blend of Claim 22 in the form of a molded or extruded article.

31.   A method of preparing a composition from a thermoplastic
35   molding polymer, an ethylene polymer; an ethylenically unsaturated

-127-

functionalized organic compound; and a reactive thermoplastic polymer, comprising:

      (1) forming a branched block ethylene polymer by

          a) adding the ethylenically unsaturated functionalized

5   organic compound to the ethylene polymer to form a branched ethylene polymer, and thereafter

          b) reacting the reactive thermoplastic polymer with the residue of the ethylenically unsaturated functionalized organic compound; and thereafter

10   (2) blending the branched block ethylene polymer with the thermoplastic molding polymer.

      32. The method of Claim 31 wherein the ethylene polymer is a homogenous ethylene polymerhaving:

15   (i) a polydispersity of less than about 3.0;

      (ii) a density of about 0.93 g/cm^3 or less;

      (iii) a a Short Chain Branching Distribution Index of greater than about thirty percent; and

      (iii) a single melting peak as determined by differential

20 scanning calorimetry between -30°C and 150°C;

      33. The method of Claim 31 wherein the reactive thermoplastic polymer is reacted with the branched narrow ethylene polymer in the presence of a catalyst selected from an alkali metal or alkaline earth

25 metal salt having a pKa of 7 or more, and a nitrogen-containing organic base.

      34. The method of Claim 31 wherein (a) the formation of the unsaturated functionalized organic compound into a branch off of the

30 ethylene polymer, (b) the reaction of the reactive thermoplastic polymer with the branched ethylene polymer, and (c) the blending of the branched block ethylene polymer with the blending or molding thermoplastic resin are all performed in a single pass through one extruder.

35

35. The method of Claim 31 wherein a branched ethylene polymer and the reactive thermoplastic polymer are fed together into an extruder, and the blending or molding resin is fed through a downstream port during the same pass through said extruder.

1 / 2 1

FIG. I

2 / 2 1

FIG. 2A

Complex Viscosity (Poise) vs Freq (rad./sec.)

□ ITP   ○ ITPg MAH
◇ ITP-PBT   △ ITP g MAH-PBT

FIG. 2B

Tan Delta vs Freq (rad./sec.)

□ ITP   ○ ITPg MAH
◇ ITP-PBT   △ ITP g MAH-PBT
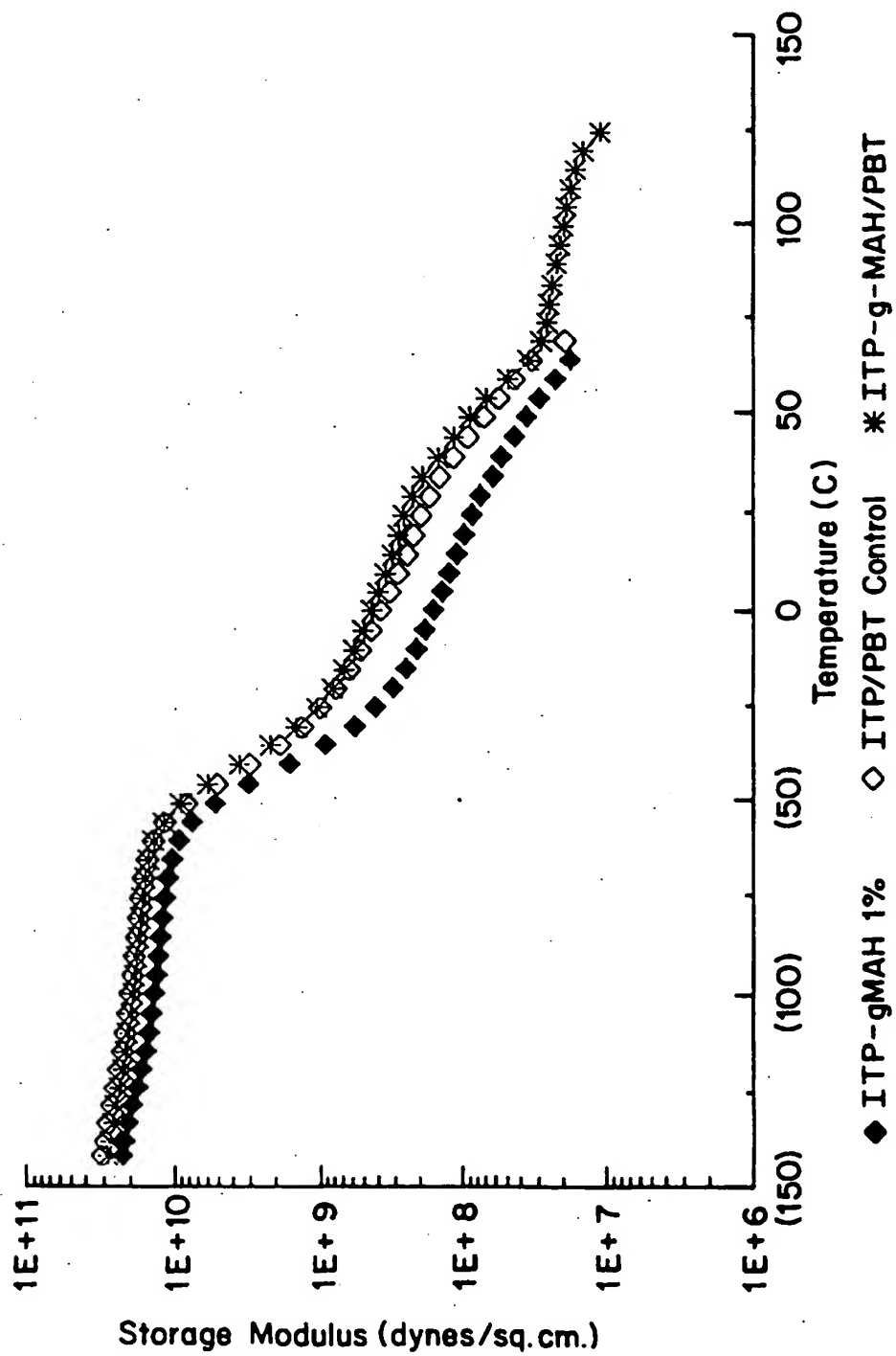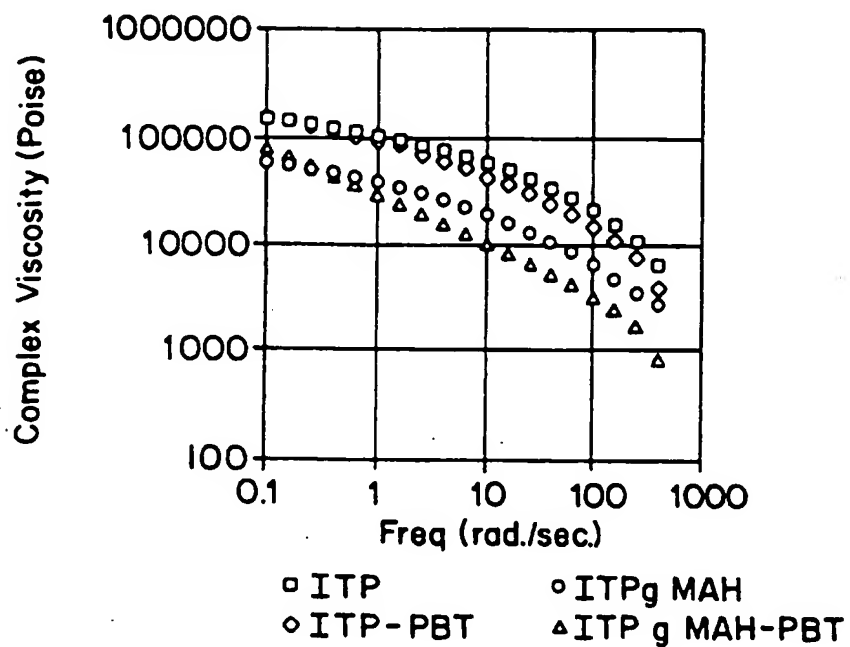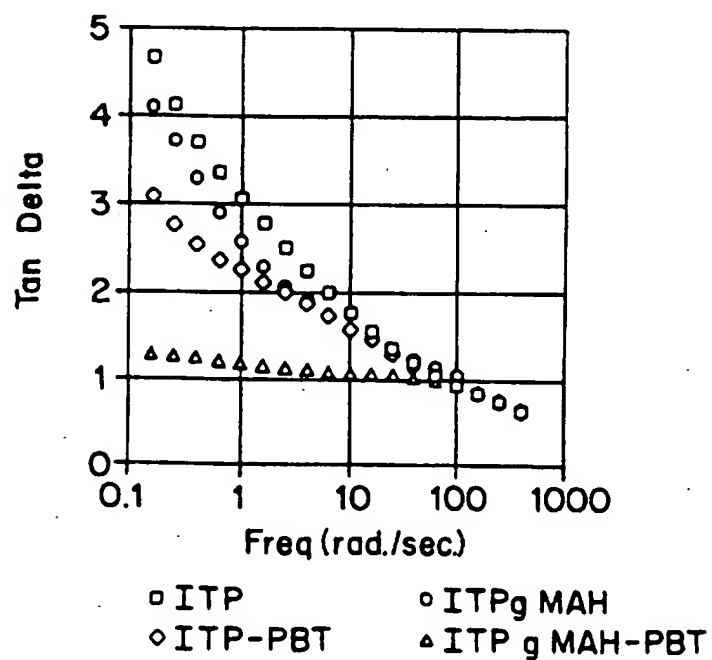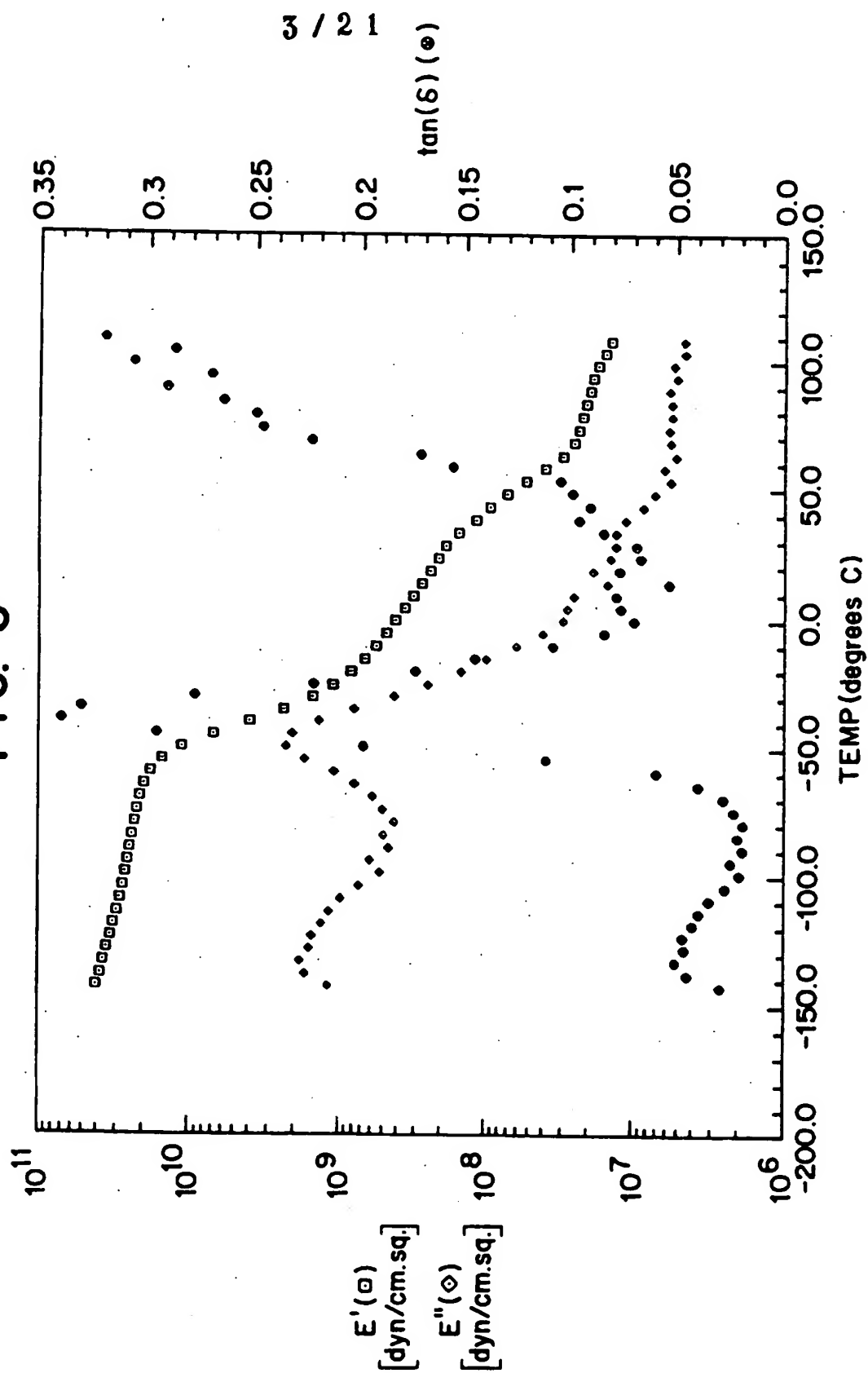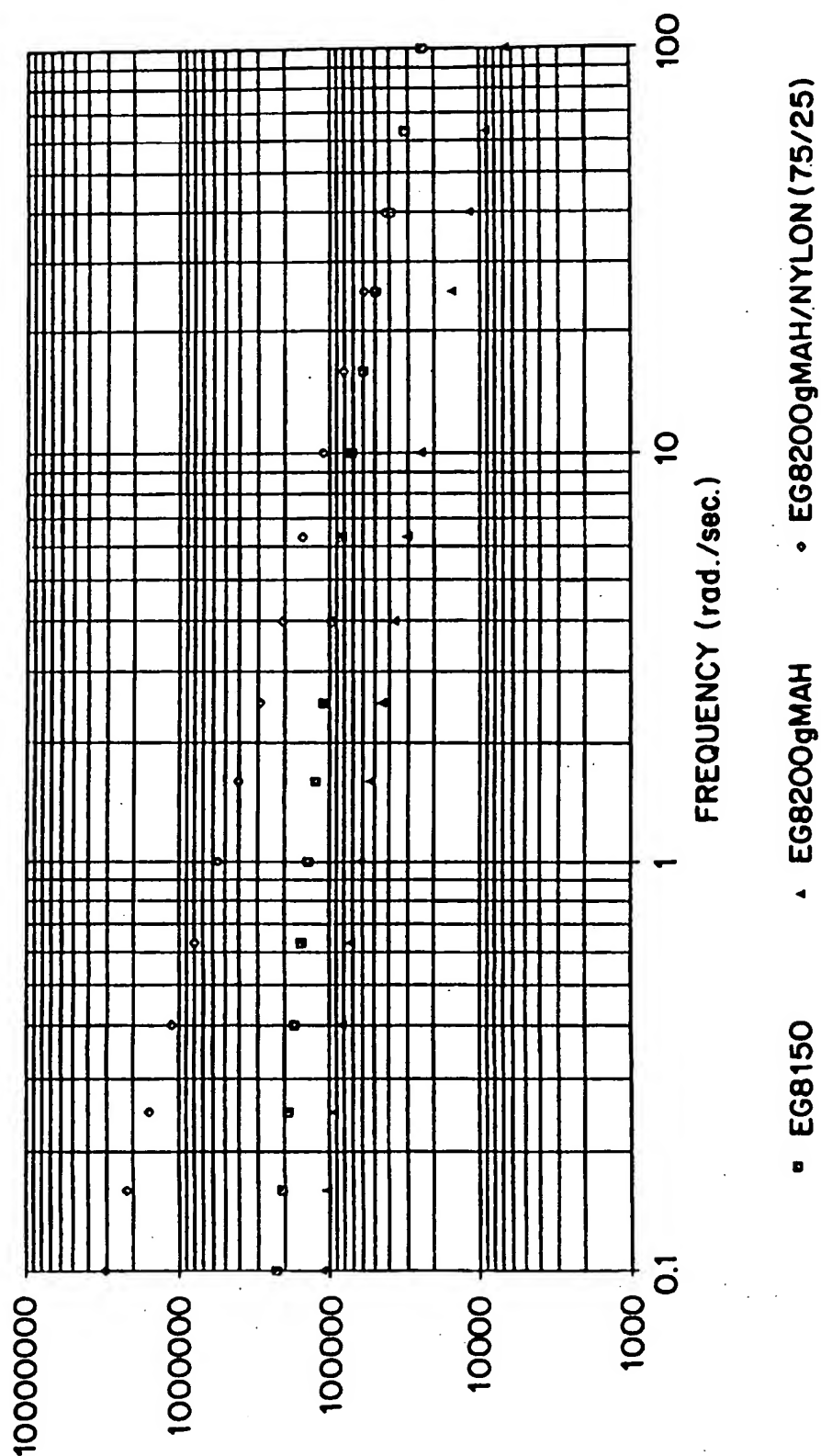
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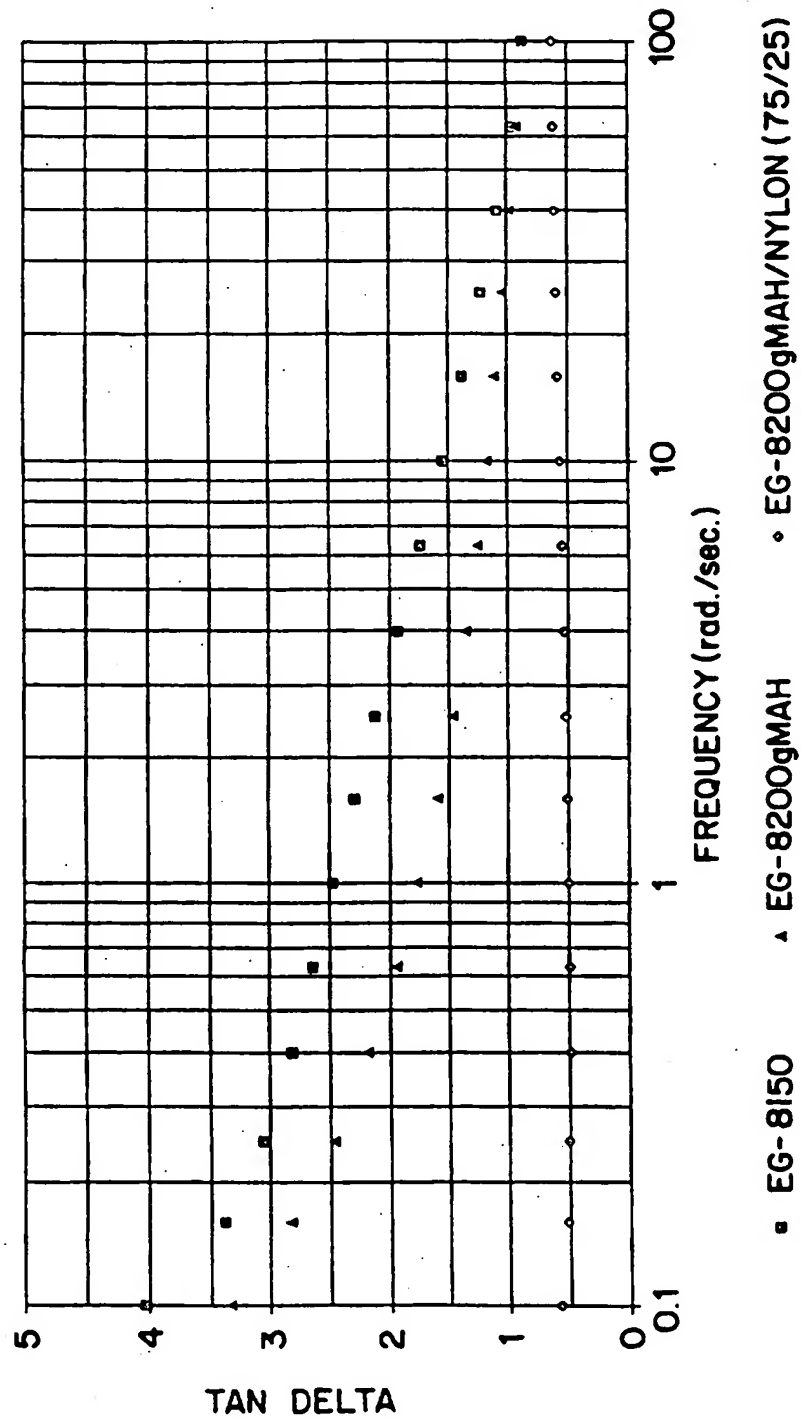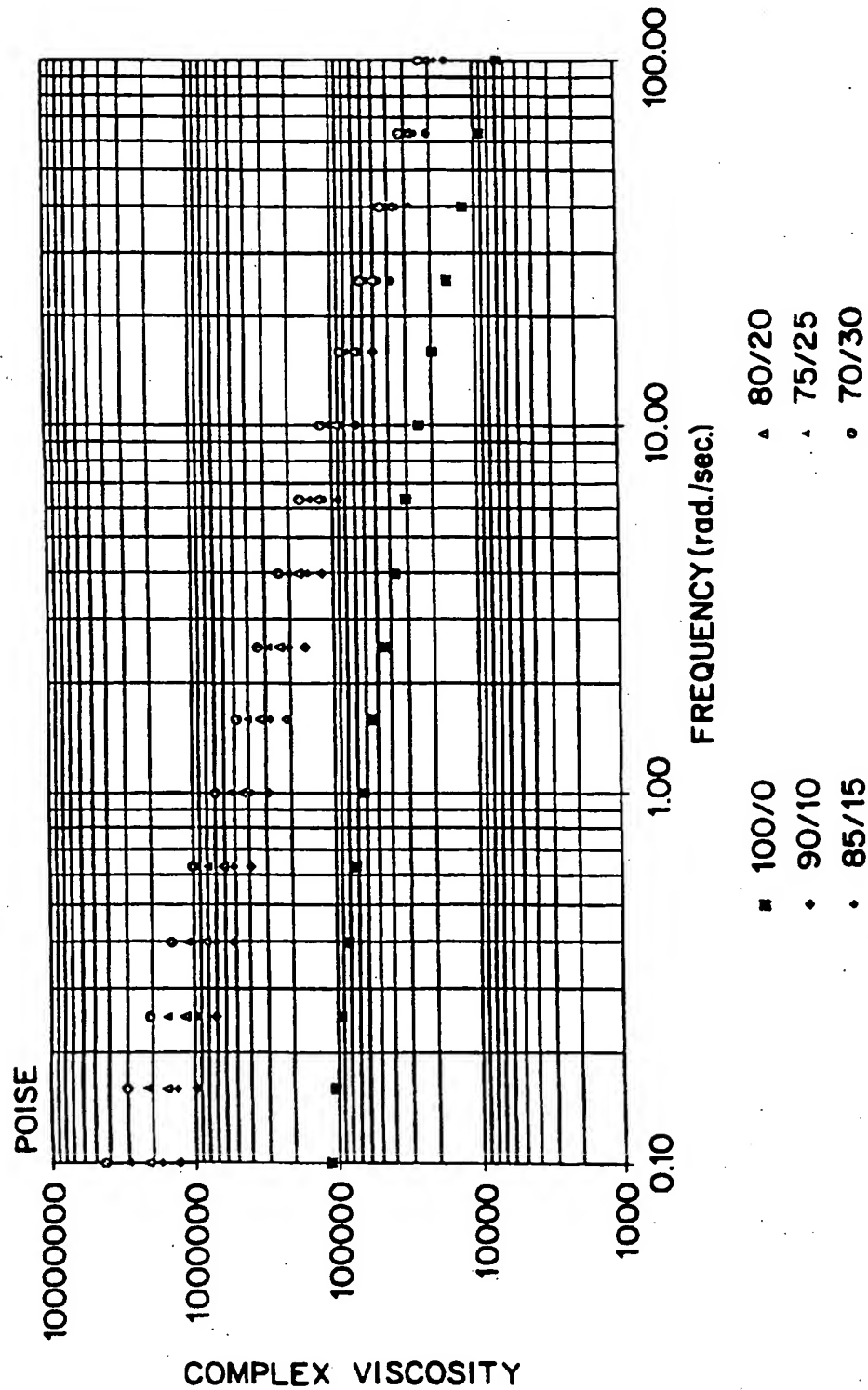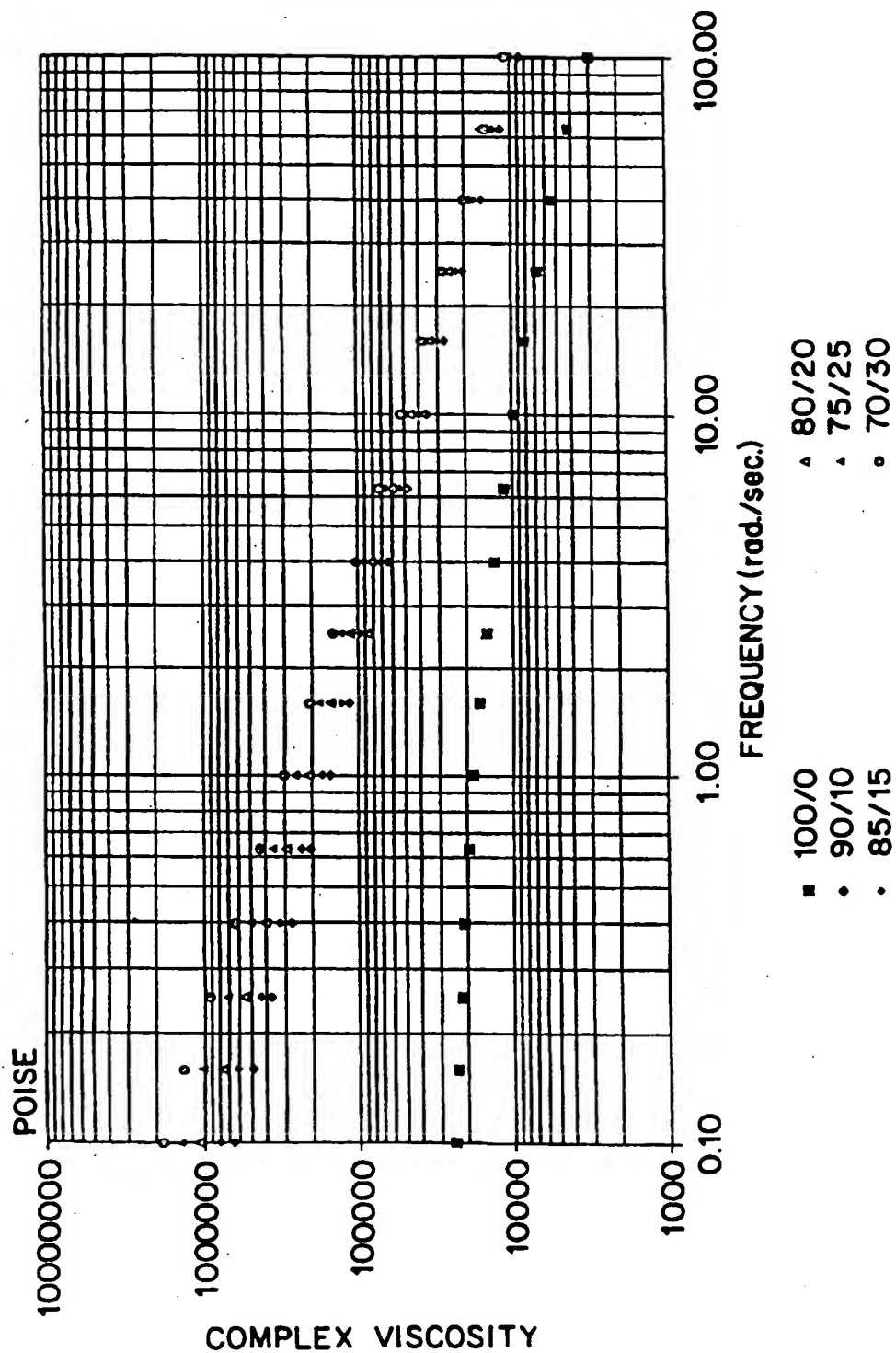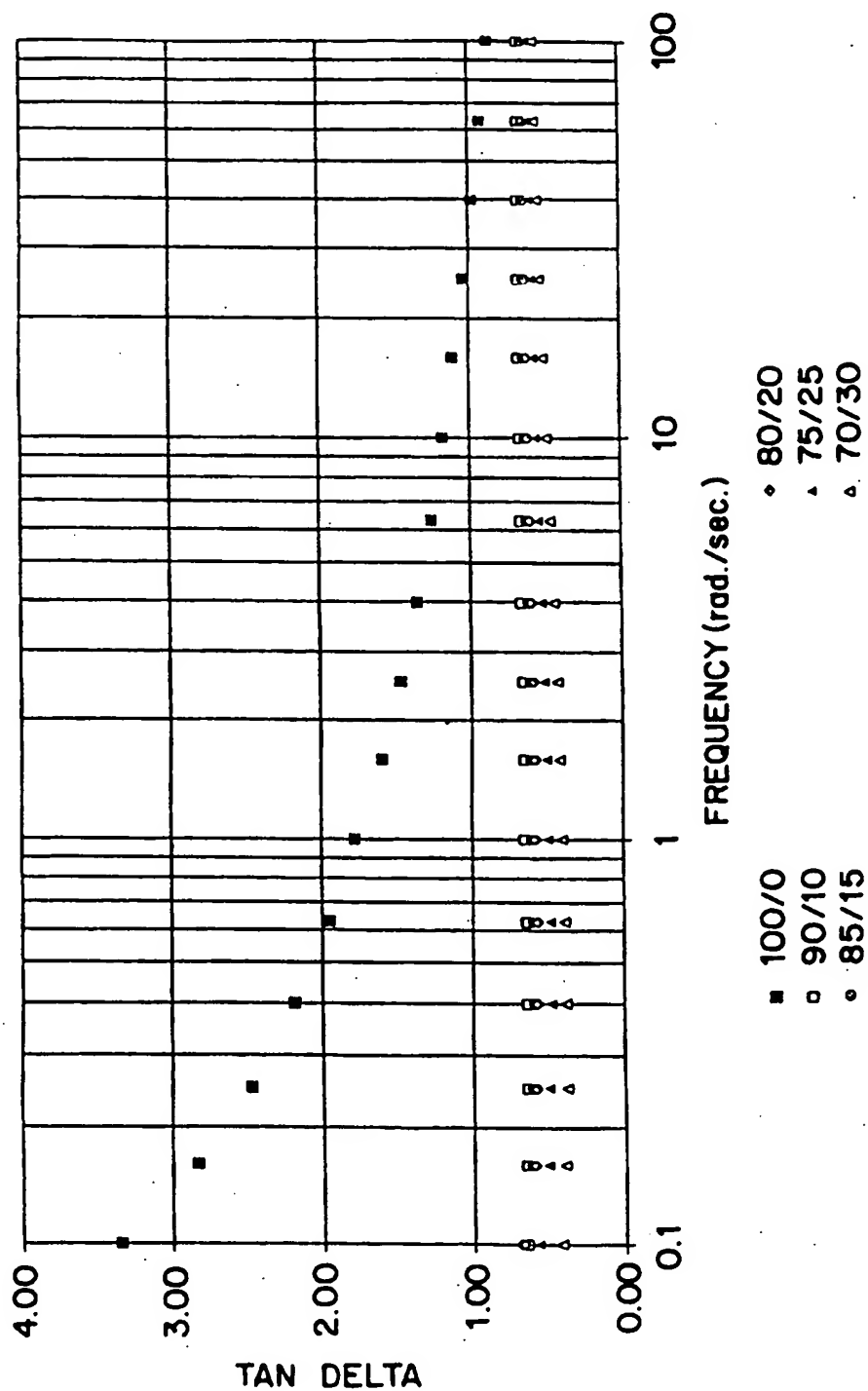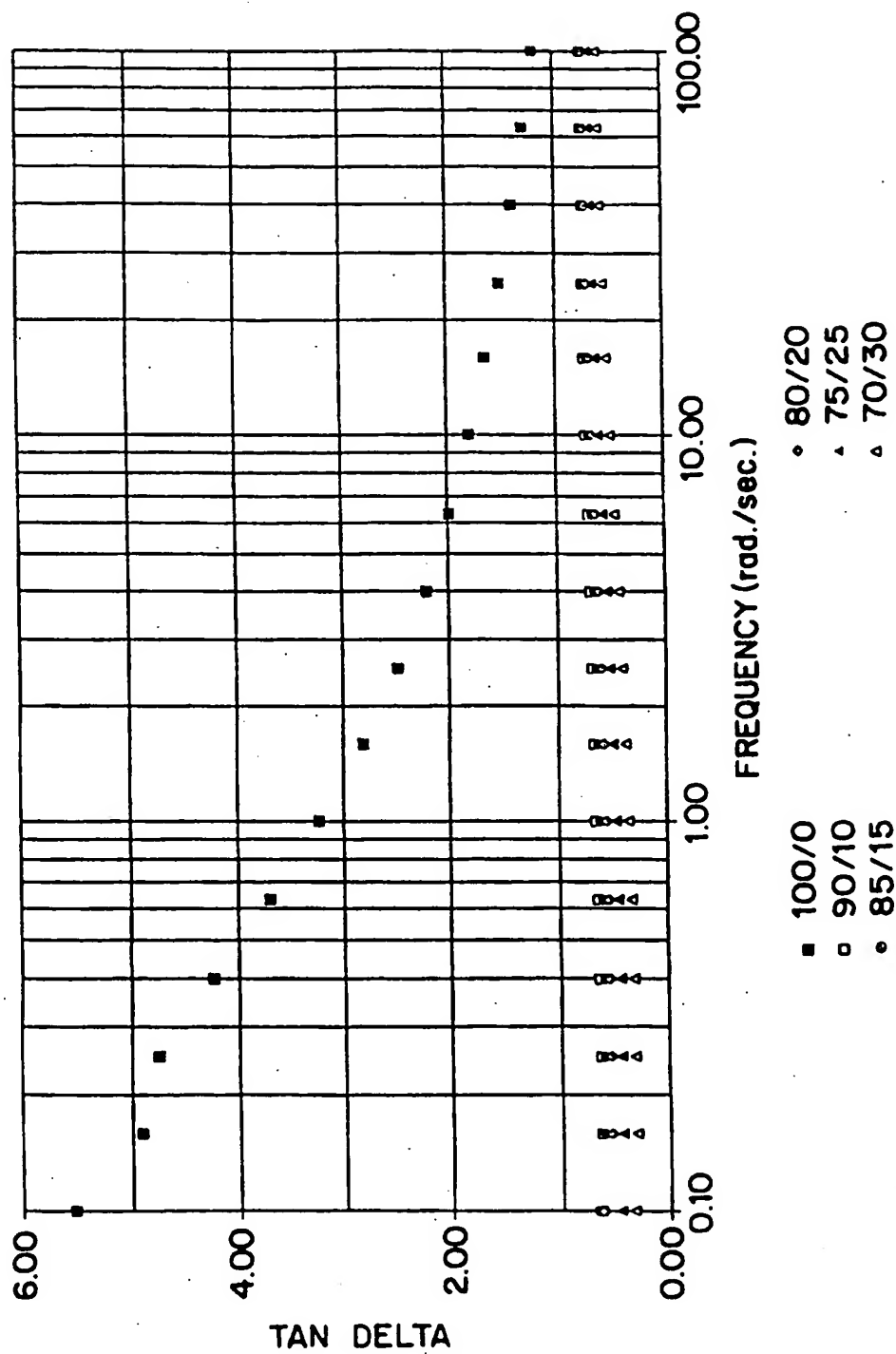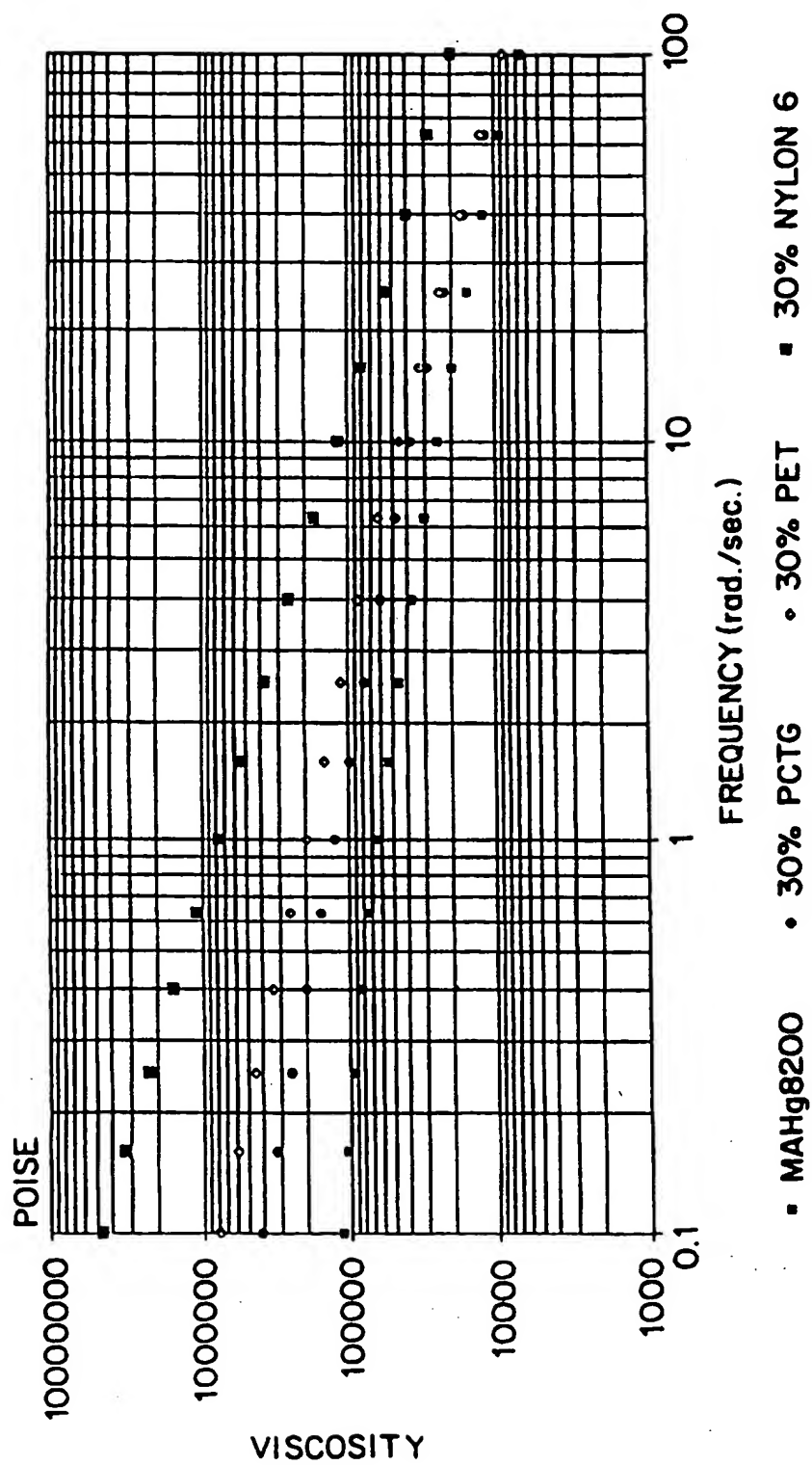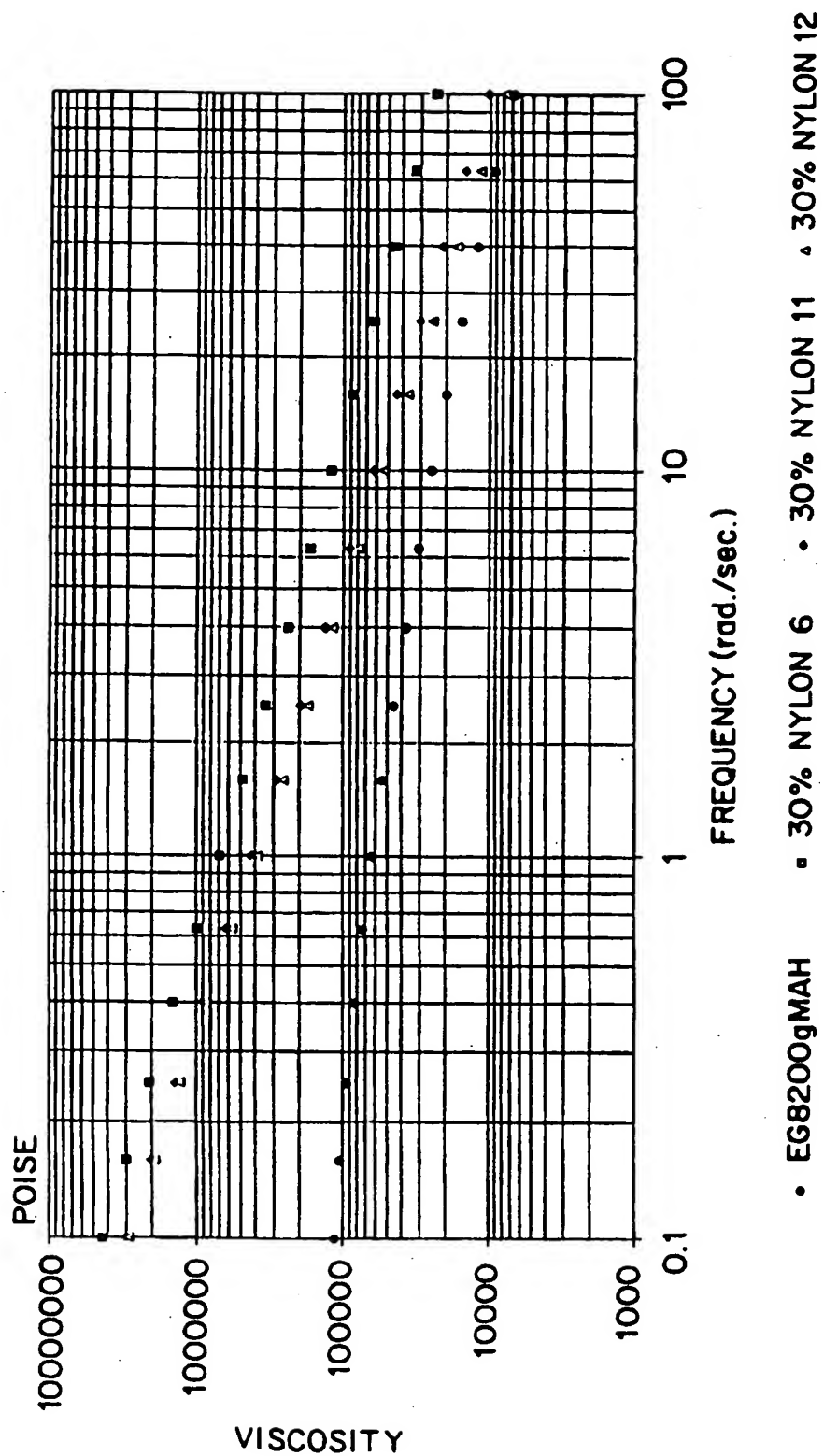
FIG. 3

FIG. 4

FREQUENCY (rad./sec.)

COMPLEX VISCOSITY

▫ EG8150　　　▲ EG8200gMAH　　　◇ EG8200gMAH/NYLON (75/25)

FIG. 5

FIG. 6

FIG. 7

FIG. 8

FIG. 9

FIG. 10

POISE

VISCOSITY

FREQUENCY (rad./sec.)

■ MAHg8200　　● 30% PCTG　　♦ 30% PET　　○ 30% NYLON 6

FIG. 11

FREQUENCY (rad./sec.)

VISCOSITY

POISE

- EG8200gMAH
- 30% NYLON 6
- 30% NYLON 11
- 30% NYLON 12

FIG. 12
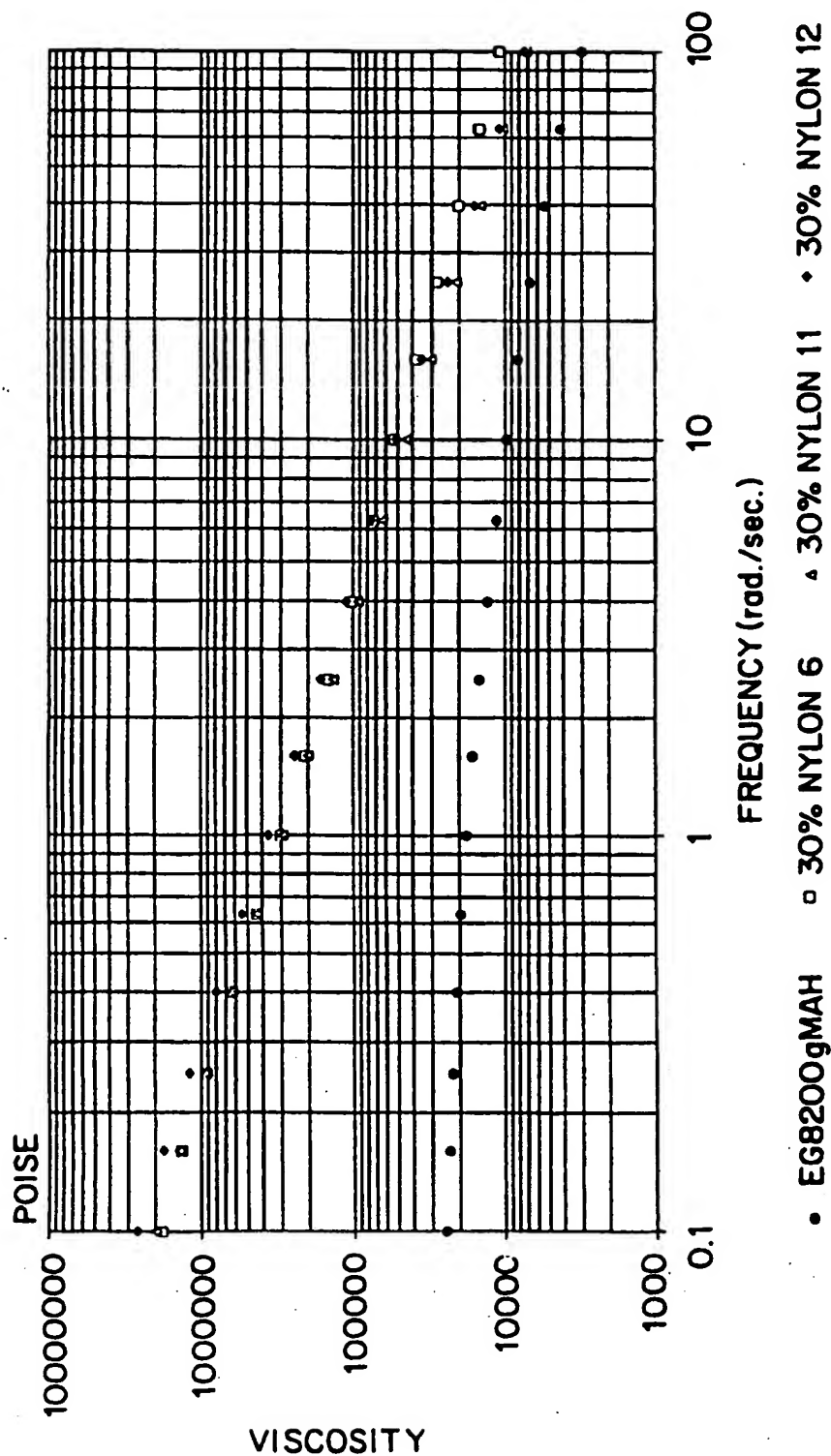
FIG. 13
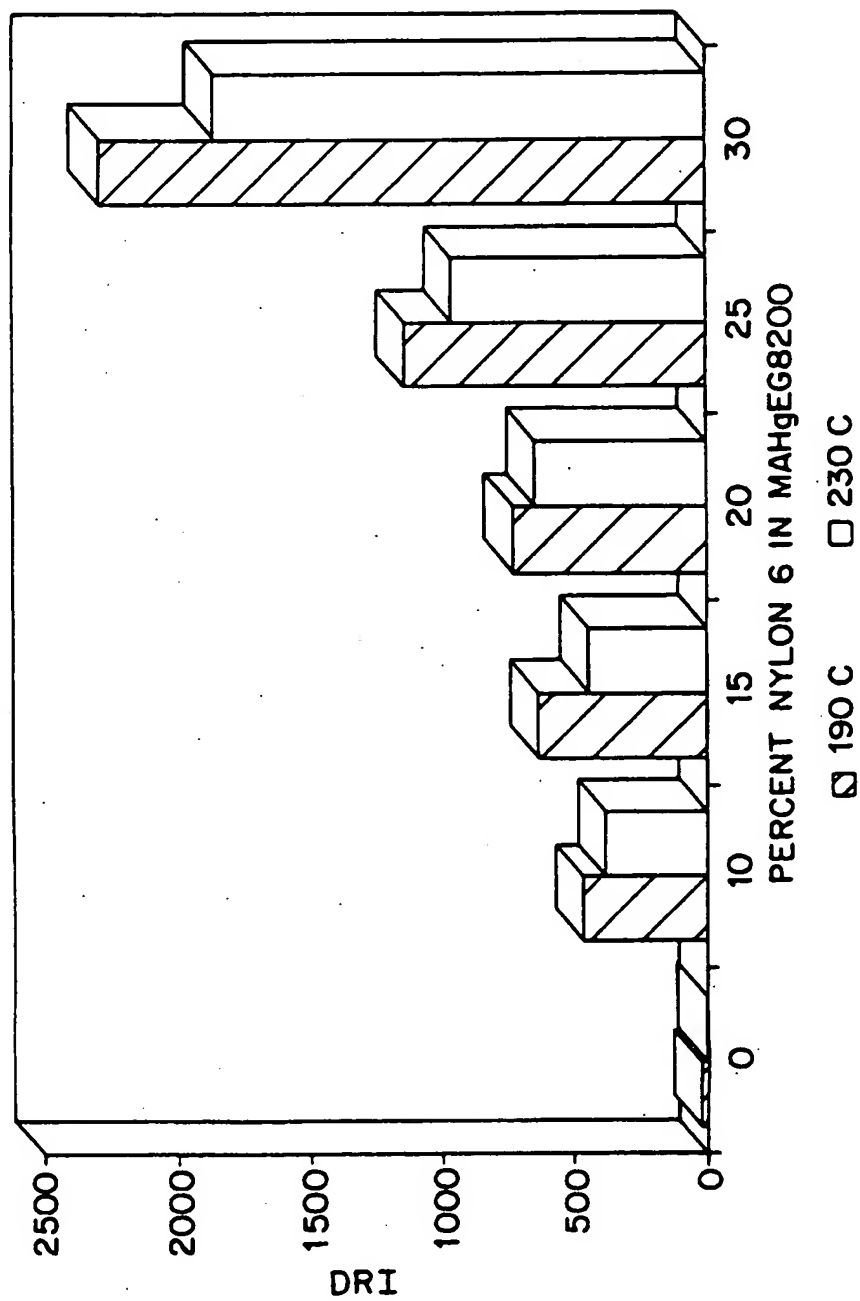
FIG. 14
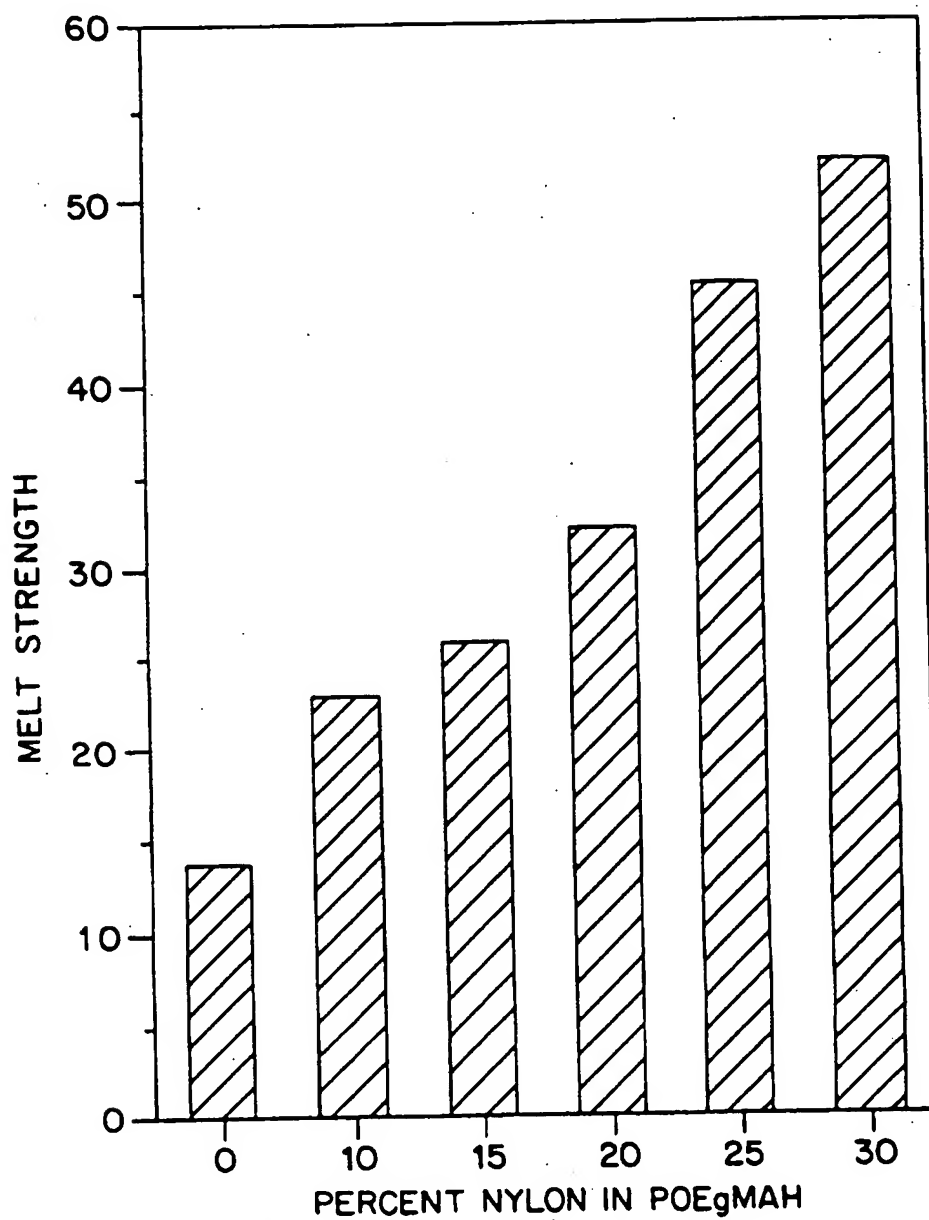
FIG. 15
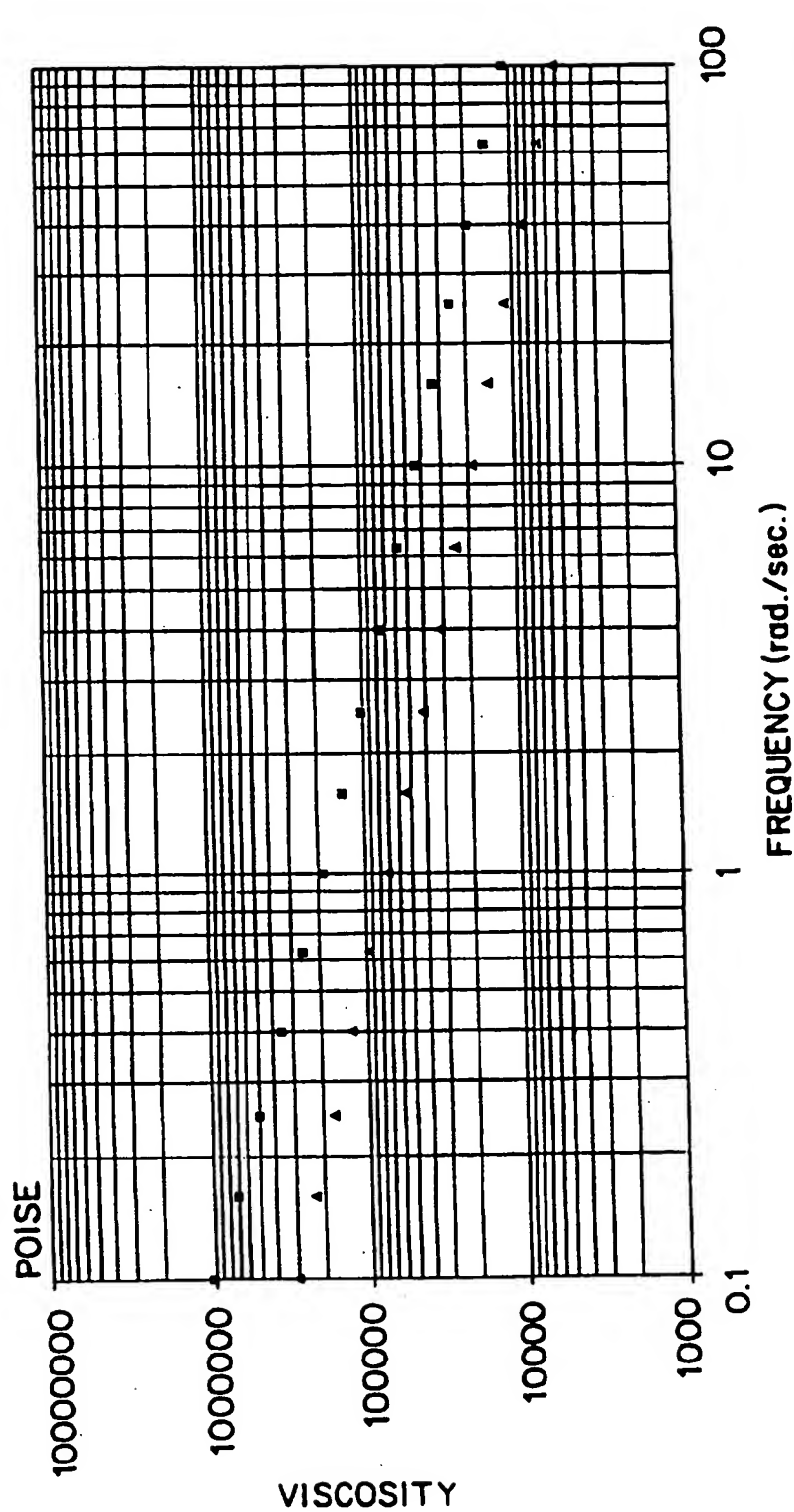
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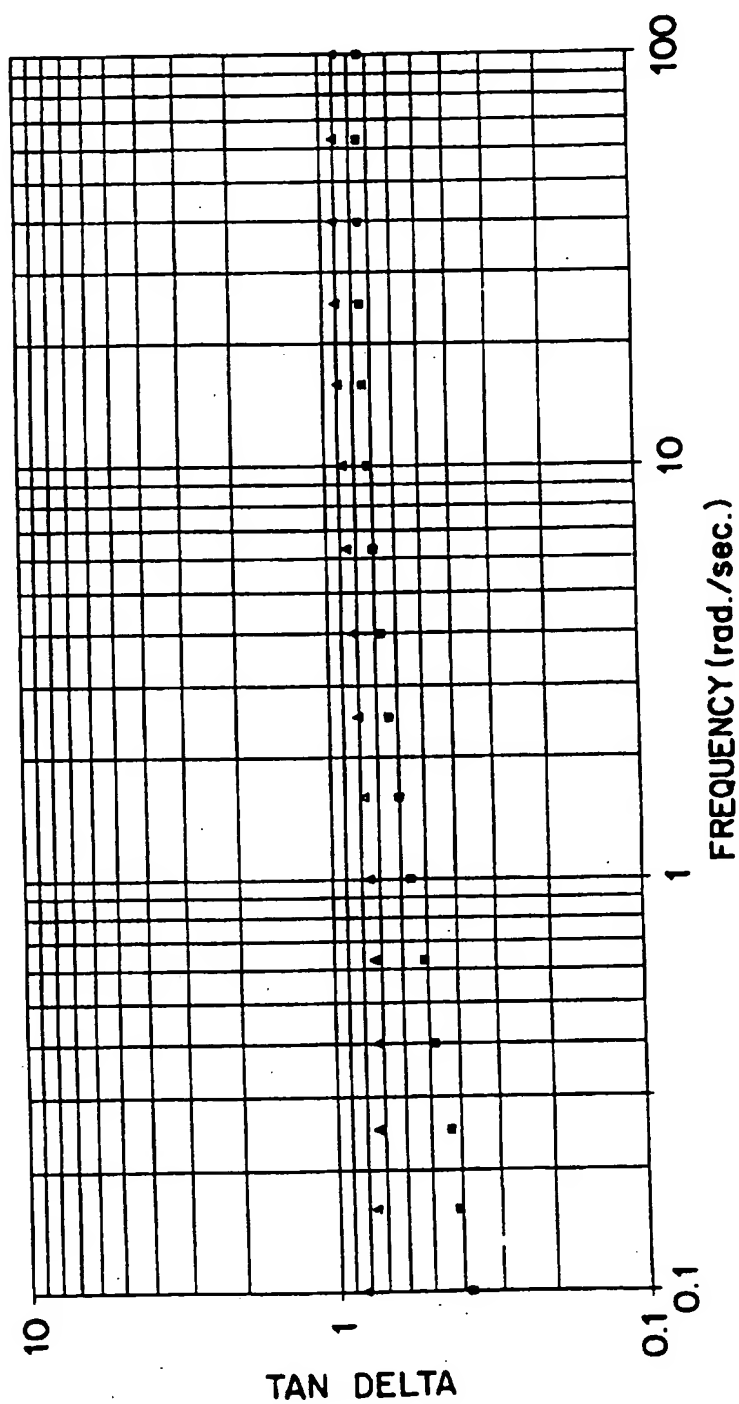
FIG. 17
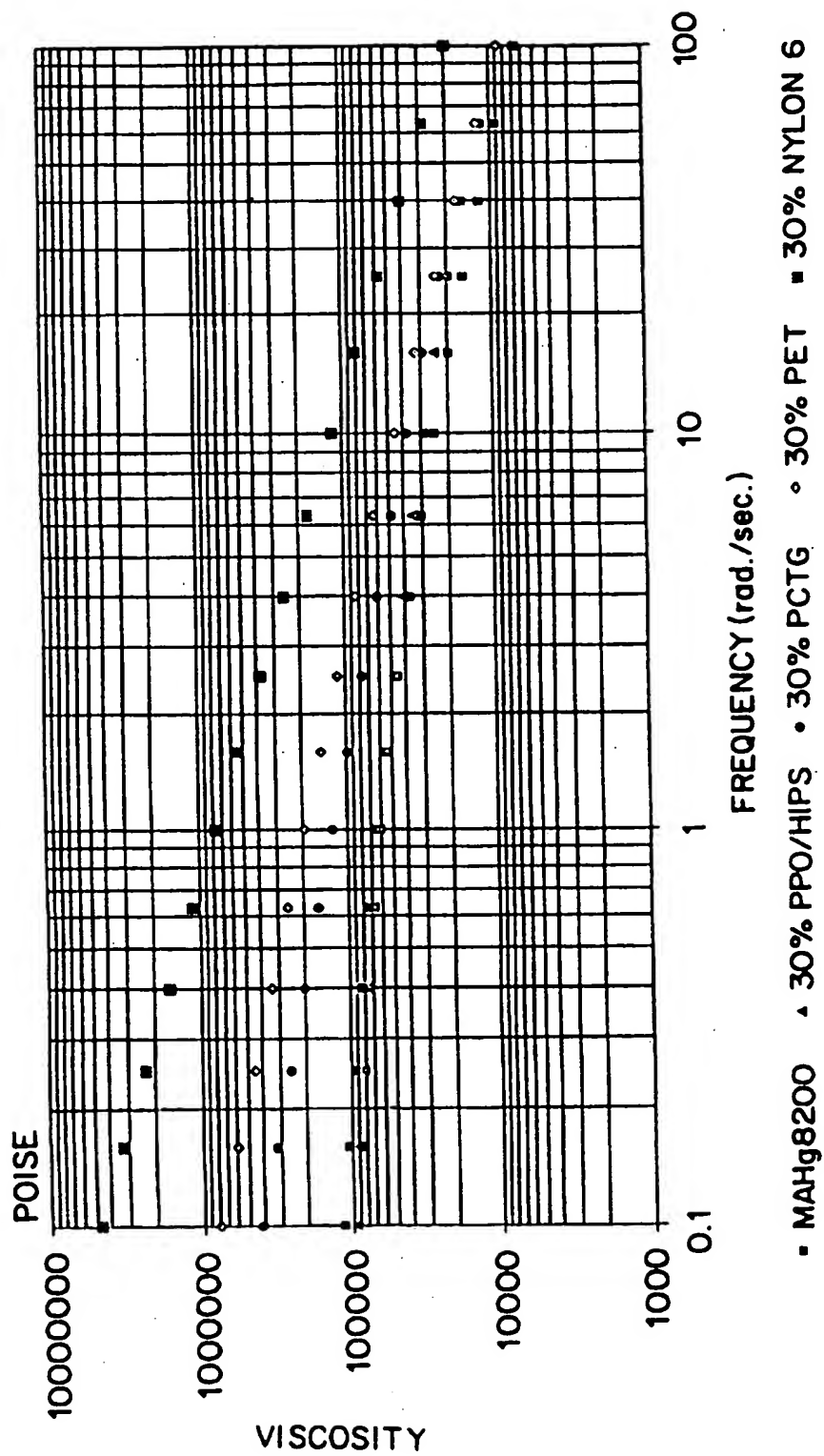
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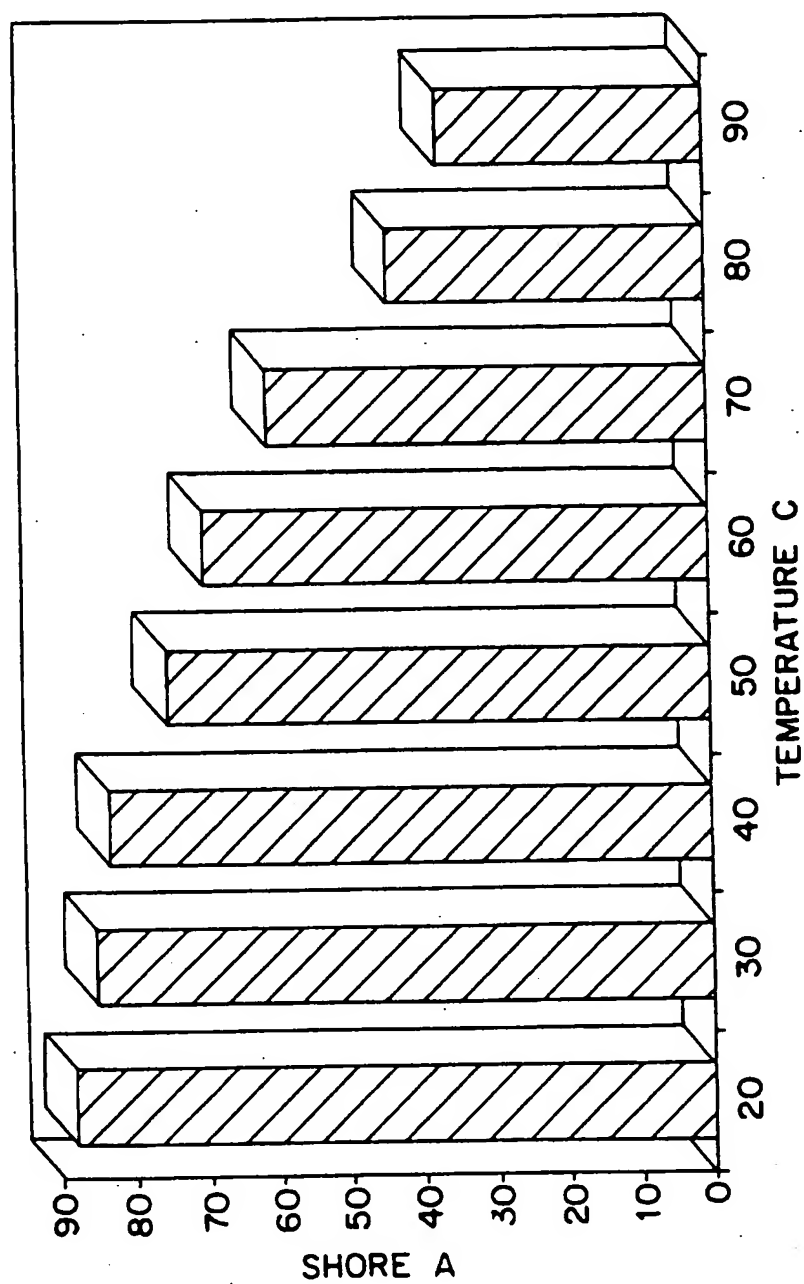
FIG. 19

Sample	Max Strain(%)	Max. Stress(PSI)	Toughness(in-lb/in)
ITP-g-MAH/PBT	2000	2700	29400
ITP*	1800	1600	14800

*Ethylene octene copolymer with 1 MI and density of 0.87g/ml
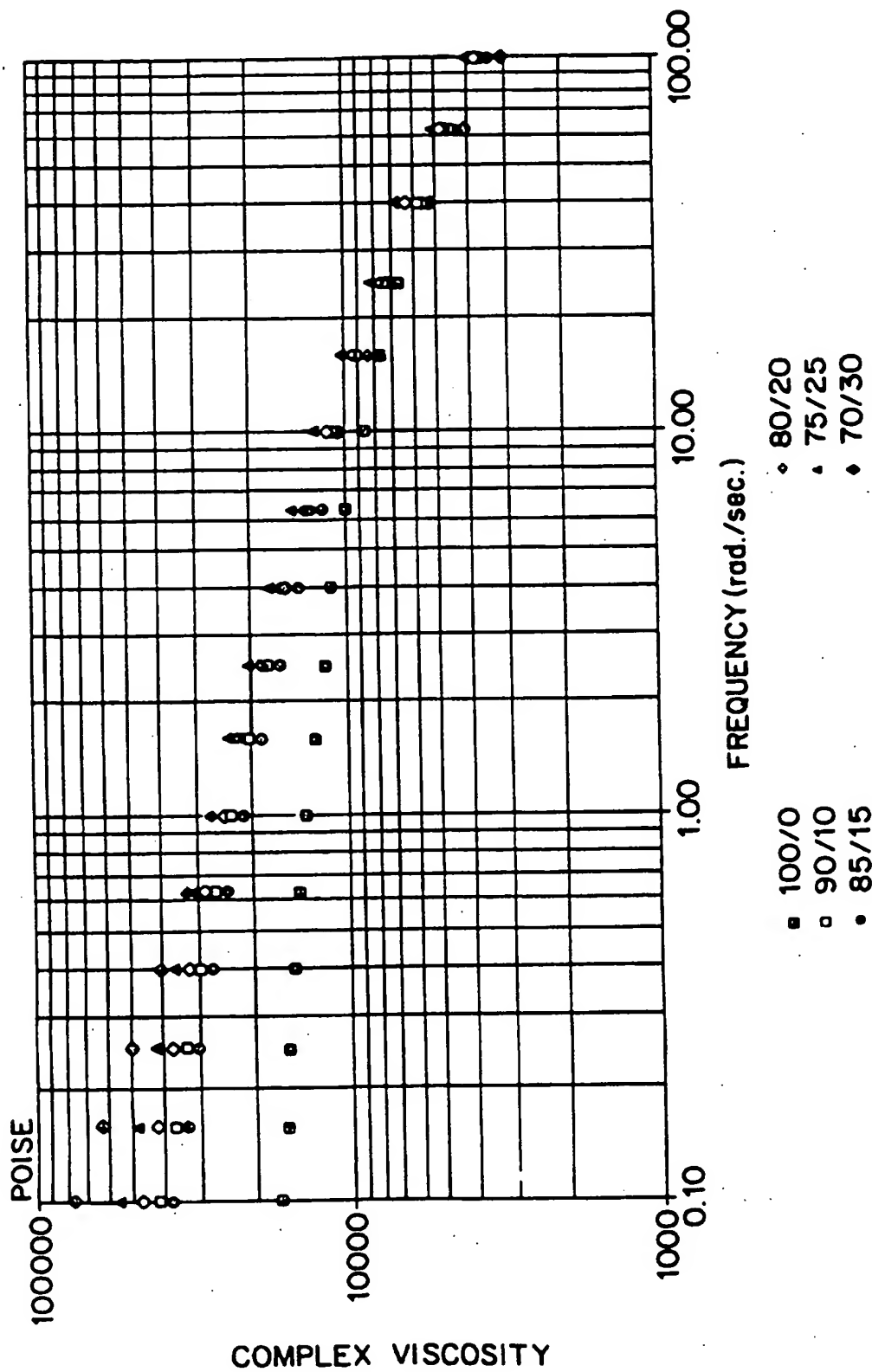
FIG. 20

COMPLEX VISCOSITY

POISE

100000

10000

1000

FREQUENCY (rad./sec.)

0.10

1.00

10.00

100.00

■ 100/0
□ 90/10
• 85/15

◇ 80/20
▲ 75/25
♦ 70/30

FIG. 21

FREQUENCY (rad./sec.)

▲ 70/30   ▲ 75/25   ● 80/20   ◇ 85/15   □ 90/10   ■ 100/0

TAN DELTA
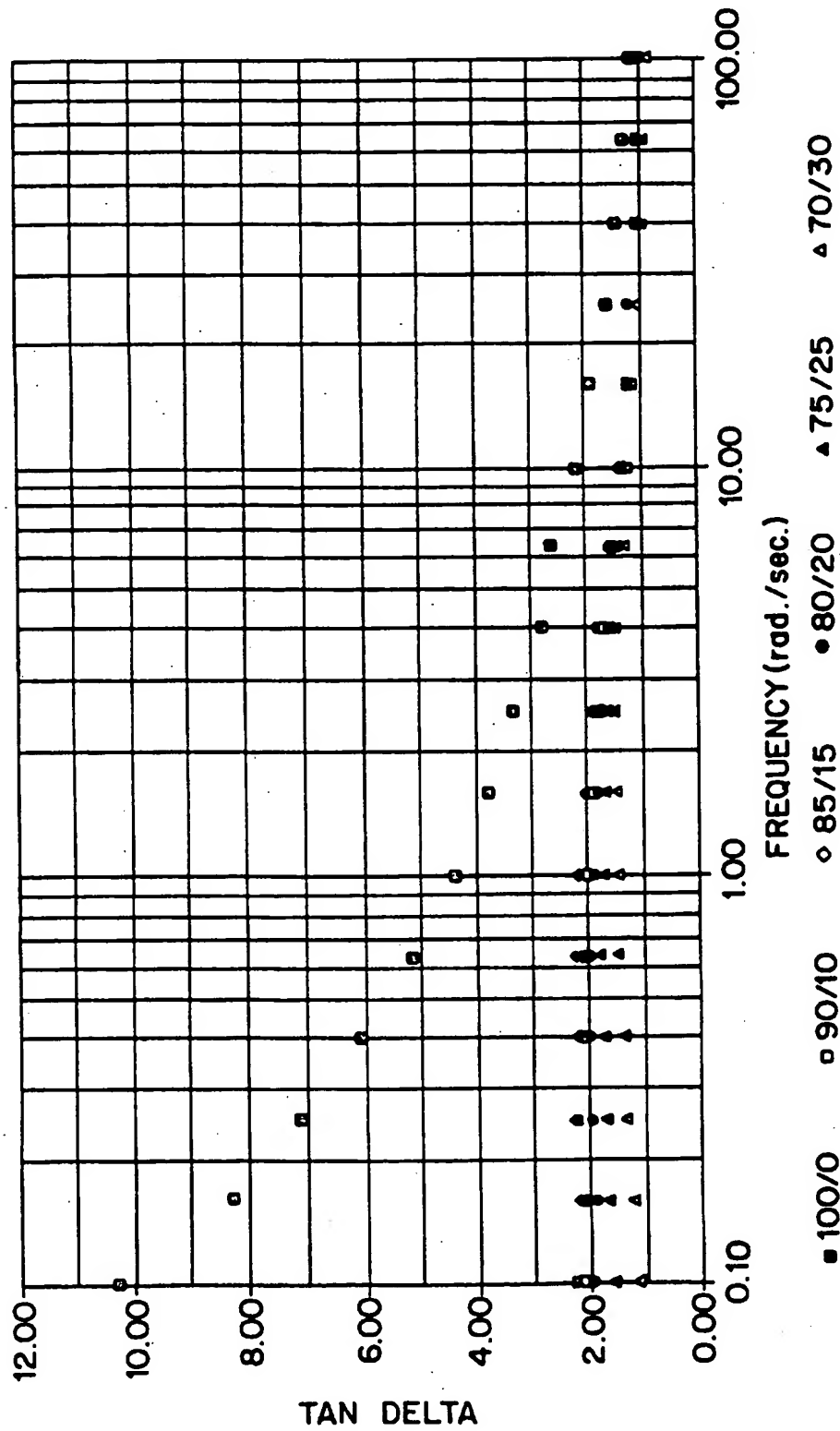
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C08F8/00   C08G81/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C08F C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,95 17466 (BOREALIS HOLDING A/S) 29 June 1995 see the whole document ---	1-35
Y	EP,A,0 492 976 (POLYPLASTICS CO., LTD.) 1 July 1992 see the whole document ---	1-35
Y	EP,A,0 186 060 (GENERAL ELECTRIC COMPANY) 2 July 1986 see the whole document ---	1-35
Y	EP,A,0 495 099 (MITSUI PETROCHEMICAL INDUSTRIES, LTD.) 22 July 1992 cited in the application see the whole document ---	1-35

-/--

[X] Further documents are listed in the continuation of box C. [X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 January 1997	10. 02. 97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Parmentier, W

Form PCT/ISA/210 (second sheet) (July 1992)

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